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# REACTOR FUEL PROCESSING

*A Quarterly Technical Progress Review*

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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## TECHNICAL PROGRESS REVIEWS

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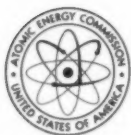
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# REACTOR FUEL PROCESSING

**A REVIEW OF RECENT DEVELOPMENTS**

Prepared for U. S. ATOMIC ENERGY COMMISSION  
by ARGONNE NATIONAL LABORATORY



- JULY 1961
- VOLUME 4
- NUMBER 3

## *foreword*

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This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Office of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., A. A. Chilenskas, I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, J. Royal, J. H. Schraidt, A. Schneider, W. B. Seefeldt, V. G. Trice, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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## Section

I

## COMMERCIAL ASPECTS OF FUEL PROCESSING

### *Industrial Participation in Fuel Processing*

Additional information has become available on the study of a privately owned fuel-processing plant by the Davison Chemical Division of W. R. Grace and Company. Some details of the plant were discussed in the previous issue of this Review.<sup>1</sup> The study selected the aqueous Purex process as the only practical multipurpose process available. Capital costs for the 1-ton-per-day plant were \$21,850,000. Direct operating costs were dependent on the processing days of fuel load available to the plant. At 200 days per year, total operating costs including capital charges were \$21,000 per day. At 300 days the costs would be less than \$18,000 per day.<sup>2</sup>

For comparison, the cost for the U. S. Atomic Energy Commission (AEC) hypothetical plant (of about the same capacity) used to determine AEC charges for processing fuels from private power reactors is \$20,500,000. At 300 days per year, the AEC daily charge<sup>3</sup> is \$15,300. However, after 1964, AEC processing charges could be in excess of \$18,000 per day due to the built-in escalation of AEC charges. The charges for fuel-processing services by AEC are admittedly not the actual costs since they were developed on a hypothetical plant.

Davison has prepared a new proposal for the operation of a privately owned plant, and the utility members of the Industrial Reprocessing Group (IRG) are currently studying the proposal. Some industry spokesmen are urging the AEC to put off expansion of AEC-owned fuel-processing facilities and, instead, store spent power-reactor fuels until private industry has an economic incentive to build processing facilities. Any additional government invest-

ment might further postpone the day when it will become economic to establish privately owned processing plants.

A major new company, called United Nuclear Corporation, has recently been formed to carry out services in the nuclear field. The three participating members of the new company are Olin Mathieson Chemical Corporation, Mallinckrodt Chemical Works, and the Nuclear Development Corporation of America. The decision to form the company, which will employ 1400 persons, was based on the following considerations, with a notable emphasis on processing spent fuel:

1. Interest by electric power utilities and the government in obtaining a wider range of nuclear services from a single integrated organization.
2. A growing demand for separated fission-product isotopes for compact nuclear power sources for military and space projects and commercial applications.
3. A growing need for spent-fuel-element processing for recovery of fissionable materials, isotopes, and other irradiated materials.
4. The AEC's expressed desire to induce private industry to enter areas, such as spent-fuel processing, which have been mainly the province of the government.<sup>4</sup>

New York State's Office of Atomic Development recently invited industrial expressions of interest for operation of a proposed state-owned Nuclear By-product Concentration and Storage Site. Twenty companies have responded to the invitation. The Office of Atomic Development specified that it would give particular weight to proposals from firms intending to conduct research or manufacturing activities at or near the site, in fuel production, spent-fuel

processing or storage, or by-product utilization. The state legislature has appropriated \$300,000 for acquisition of such a site, and three alternative locations are under consideration in the western part of the state where there are underground salt formations.<sup>4,5</sup>

The preliminary design of a thorium- $U^{233}$  pilot plant has been completed by Allis-Chalmers Manufacturing Company for Italy's National Committee for Nuclear Energy (CNEN) under a four-year program to delineate the technical feasibility and economic advantages of the thorium fuel cycle. A development program is under way in support of the design, based on the Thorex solvent-extraction process, and includes reactor evaluation to provide the Italians with the background to select a suitable line of thorium-burning reactors. Operation of the processing pilot plant is expected by mid-1963. Fuel elements to be processed will come from the Elk River Reactor designed by Allis-Chalmers. Capacity of the pilot plant will be 15 kg of thoria per day containing 4 per cent uranium dioxide. Outside dimensions of the complete plant are 150 by 75 ft. A 35- by 15-ft hot cell will feature a unique method of mounting, operating, and maintaining hot process equipment by a mechanical system of movable racks. Should a piece of equipment become inoperable, the rack holding it would be removed to a decontamination and repair cell.<sup>6</sup>

### *Fuel-Cycle Costs*

In recent months a number of statements and suggestions pertaining to the costs of the nuclear reactor fuel cycle have been made by members of the nuclear industry. Any substantial reduction in fuel-cycle costs could be a strong encouragement to the development of nuclear power. It has recently been suggested, in an analysis of fuel-cycle costs in relation to over-all nuclear power costs, that the former cannot exceed 1 to 2 mills/kw-hr if reactors are to be economic.<sup>7</sup>

Several recommendations regarding the AEC's uranium procurement program have recently been made. Among these was the suggestion that the possibility of some integration of uranium milling operations with feed materials production should be reviewed as a means to reduce costs. Expensive steps of precipitating, drying, and packaging uranium

ore concentrates might thereby be eliminated, as well as the cost of redissolving the concentrates in preparation for production of feed materials in uranium refinery plants such as those at Fernald, Weldon Springs, and Metropolis.<sup>8</sup>

Improvements in processes for production of uranium ore concentrates by new solvent-extraction methods suggest the possibility that very high grade concentrates might be produced at the mills if an economic incentive existed. Improvement in concentrate purity might allow substantial simplification of the final refining operations, particularly if specifications for power-reactor-grade uranium can be relaxed. The possibility of producing crude uranium tetrafluoride at the mills for feed to the fluoride refining process used at Metropolis might also be considered.

### *Financial Protection for Fuel Processors and Fabricators*

The AEC has published in the *Federal Register* an invitation for public comment on whether Price-Anderson indemnity protection should be extended to licensed fuel fabricators and processors. Such protection would apply to nuclear incidents occurring at the facilities of these licensees. The indemnity provided would apply only to public liability claims exceeding the levels of financial protection which the AEC would require these licensees to maintain. Any decision to extend indemnity protection would involve primarily firms offering fuel-fabricating services.<sup>9</sup>

In the case of privately owned fuel-processing services, the matter of financial protection is reflected by a recent AEC decision concerning the Martin Company. This firm was recently authorized to construct a facility, to be known as the Martin Radioactive Materials Laboratory, at Quehanna, Pa., to process material for isotopic power sources. Because this will involve the separation and storage of small amounts of plutonium, the plant is considered a "production facility," defined in AEC regulations as any facility designed or used for the processing of irradiated materials containing special nuclear material. Such operations are required by the Atomic Energy Act to maintain financial protection as specified by the AEC and to enter into agreement for additional federal indemnification.

Interim financial requirements were arrived at by comparing the maximum inventory of radioactive material being processed in a single step of the Quehanna operation with the amount of radioactive material in a nuclear reactor. On this basis the required financial protection<sup>10</sup> was set at \$3,500,000.

### Radioisotope Production

The new Martin production facility mentioned in the previous section is to make isotopic sources of electric power for use in the AEC's

is currently favorable compared with other isotopes. AEC projected future estimates, based on construction of a major separation facility, indicate that the separated fission products, Ce<sup>144</sup> and Sr<sup>90</sup>, would have the lowest costs.<sup>12</sup>

Scientists interested in studying the origin of matter would like to guard against the contamination of the natural radioactivity of other bodies in the solar system by activity transported from earth. Curium-242 is advantageous from this standpoint since it has never been found in meteorites or in spectroscopic observations within the solar system.<sup>13</sup> Since

Table I-1 TYPICAL RADIONUCLIDE HEAT SOURCES<sup>12</sup>

Nuclide	Mode of decay	Half life	Fuel form	Density, g/cm <sup>3</sup>	Thermal power, watts/cm <sup>3</sup>	Fuel required, curies/watt	Estimated costs, \$/watt	
							Current	Projected
Po <sup>210</sup>	Alpha	138 days	Po	9.3	1320	31.2		
Cm <sup>242</sup>	Alpha	162 days	Cm <sub>2</sub> O <sub>3</sub>	11.75	1169	27.2	80*	45*
Pu <sup>238</sup>	Alpha	86.4 years	PuC	12.5	6.9	30.3		1600
Ce <sup>144</sup>	Beta	285 days	CeO <sub>2</sub>	6.4	12.5	128	87	14†
Pm <sup>147</sup>	Beta	2.6 years	Pm <sub>2</sub> O <sub>3</sub>	6.6	1.1	2700	3000	1630†
Cs <sup>137</sup>	Beta	33 years	CsCl	3.9	1.27	320	500	54†
Sr <sup>90</sup>	Beta	28 years	SrTiO <sub>3</sub>	4.8	0.54	153	455	23†

\* Irradiation cost is not included (rate of increase = \$100/watt).

† AEC estimates are based on construction of major separation facility.

Systems for Nuclear Auxiliary Power (SNAP) program. The AEC will furnish the Martin Company Sr<sup>90</sup> in batches of 100 kilocuries as a separated fission product. The Sr<sup>90</sup> will be processed by remote control in hot cells to form fuel pellets, which will be sealed inside a metal capsule for loading into a SNAP generator. Martin will also process Cm<sup>242</sup>, produced by irradiating capsules containing Am<sup>241</sup>. The capsules will be chemically processed to separate plutonium, fission products, and, if desired, the americium in order to produce curium fuel capsules. About 12 kilocuries of curium will be produced from three irradiated capsules of americium. Completion of the facility<sup>11</sup> is expected in late 1961.

In a recent article on the use of radionuclide power for space missions, the relative costs and other characteristics of various isotopes suitable for radiation-powered generators are given. As shown in Table I-1,\* the cost of Cm<sup>242</sup>

curium is an alpha emitter, it requires less shielding than the beta-gamma emitting isotopes.

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\* Table I-1 is reprinted here by permission from *Nucleonics*.<sup>12</sup>

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## Section

## II

## SAFETY IN CHEMICAL PROCESSING

### *Criticality Incident*

An incident involving an accidental criticality occurred at the Idaho Chemical Processing Plant (ICPP) on Jan. 25, 1961. The summary of the preliminary report of the investigating committee follows:<sup>1</sup>

At approximately 0950 Wednesday, January 25, 1961, a nuclear excursion occurred in a first cycle product evaporator at the Idaho Chemical Processing Plant (ICPP), National Reactor Testing Station. Radiation alarms were actuated by the prompt gamma radiation produced at the time of the nuclear excursion and from radioactive gas subsequently released through the exhaust stack to the atmosphere. All personnel (251), including construction workers, in the ICPP area evacuated to a region approximately 500 feet west of the Process Building, where the radiation level was determined to be less than 1 mr/hour.

Available evidence indicates that the state of criticality resulted from the accidental lifting of a concentrated solution of 90 per cent enriched uranyl nitrate (200 g of U/liter) from the lower, geometrically safe section of the evaporator into the upper, 24-inch diameter, critically unsafe, vapor-disengagement section. The most likely cause of the lift appears to have been a sudden burst of air inadvertently introduced into the bottom of the evaporator. The mechanism by which this could have occurred is well defined; however, no definite proof either from instrument records or direct testimony has been obtained to make this premise conclusive.

Of the 251 individuals present in the ICPP area at the time of the incident, none received significant radiation exposure. The highest exposure as determined from film badge readings did not exceed 55 millirem of penetrating radiation. Essentially zero beta radiation was detected. No significant neutron exposures or internal contamination from inhalation were found. The absence of significant exposures is attributable to the extensive shielding provided by the process cell in which the event took place and the control of the fission gases by the equipment.

High radiation levels resulting from normal operation of the equipment have precluded a detailed inspection of the evaporator or of other equipment contained in the cell. Limited inspection by means of brief observation, photographs, and subsequent flow tests indicated that there was no significant damage to equipment.

The incident occurred after the ICPP began processing highly enriched uranium-aluminum fuels, after a lengthy shutdown. This was the first hot processing in the particular equipment involved in the incident in approximately 12 months, although a cold run had been made to check equipment modifications.

The vessel in which the nuclear excursion occurred is a continuous thermosiphon evaporator. Application of heat to the tube bundle of the evaporator vaporizes part of the liquid in the tubes, discharging a mixture of liquid and vapor into a 2-ft-diameter vapor-disengaging space atop the cold leg. It was recognized during design that the vapor-disengaging space was not geometrically safe. As a safety measure a 1½-in.-diameter overflow line was provided below the 2-ft-diameter section. Overflow material is collected in geometrically safe vessels. Two pumps are provided to transfer the product solution from the evaporator to storage. In the past these pumps have required considerable maintenance due to erratic pumping rates.

Events leading to the incident included the failure of one of the pumps to deliver the product solution. An attempt was made to clear the lines by using water that was moved by air pressure. The sequence of events just prior to the nuclear excursion suggests that a burst of air was inadvertently introduced into the bottom of the evaporator in the line-clearing operation, causing the lifting of the uranium solution into the critically unsafe disengaging section. The mag-



nitude of the excursion has been estimated at  $6 \times 10^{17}$  fissions.

The evacuation of the building and outside working areas was completed in <10 min. The first reentry was made about 20 min after the evacuation had been signaled. Approval for return of all employees, based upon the absence of external contamination and radiation levels above normal, was given about 4 hr after the nuclear excursion.

Immediate steps were taken to minimize criticality hazards and to preclude the repetition of incidents of this nature.

A previous incident occurred at the ICPP on Oct. 16, 1959, in which the magnitude of the excursion was considerably larger (about  $4 \times 10^{19}$  fissions).<sup>2</sup>

### Chemical Explosion Hazards

Two recently issued reports<sup>3,4</sup> deal with the problems of chemical explosions in processes designed to recover fissionable elements from spent nuclear fuels.

In the past, violent explosions have occurred during the evaporation of aqueous systems containing traces of tributylphosphate (TBP), nitric acid, and uranyl nitrate. Accordingly, studies have been made at the Savannah River Laboratory<sup>3</sup> to determine the rate of decomposition of TBP containing nitric acid and uranyl nitrate to estimate the conditions under which the reaction becomes self-accelerating. The decomposition rate of the TBP-nitrate complex was found to be first order. The half life of the reaction was correlated by an Arrhenius equation as follows:

$$t_{1/2} = \frac{0.693}{S} e^{E/RT}$$

where  $S$  is frequency factor =  $4.3 \times 10^{10}$  in nitric acid systems and  $E$  is energy of activation = 26,800 cal/mole. The half life was independent of nitric acid concentration, the presence of salts, and suspected catalysts such as urea and ferric nitrate. Based on experimental decomposition kinetics data, temperatures were calculated at which the reaction becomes self-accelerating (initiation temperatures), as a function of area, volume, concentration, and heat-transfer coefficient. As a typical example, calculations indicated that the reaction can become self-accelerating at 120°C if a tank 8 ft in

diameter contains 0.25 ft (37 gal) of 100 per cent TBP with a concentration of nitric acid corresponding to equilibration with an aqueous phase of 10.7M nitric acid. Initiation temperatures as a function of the volume of TBP-nitrate complex for various diameter vessels are shown in Fig. II-1. In laboratory experiments that approximated an adiabatic condition, runaway reactions were demonstrated at temperatures of 130°C, but not at 125°C.<sup>3</sup>

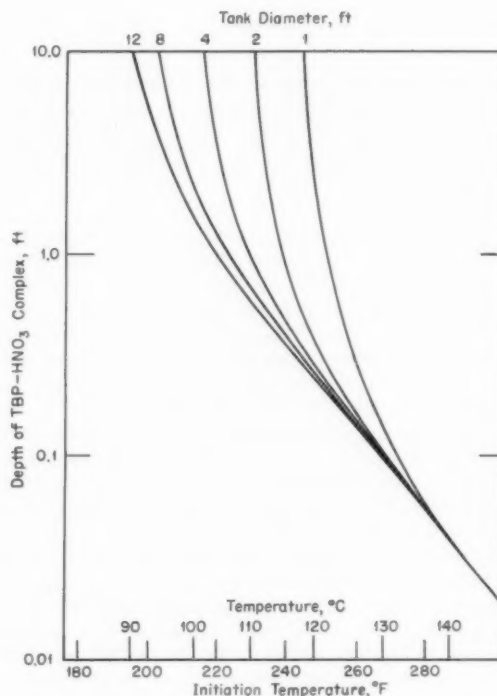


Fig. II-1 Temperature at which self-accelerating reaction occurs in TBP-uranyl nitrate-nitric acid systems.<sup>3</sup> The TBP-HNO<sub>3</sub> complex was prepared by equilibrating TBP with 10.7M HNO<sub>3</sub>.

A survey<sup>4</sup> has been carried out of the potential for vapor-phase explosions when stainless-steel-clad fuels are dissolved in dilute aqua regia (Darex process) or sulfuric acid (Sulfex process). The thermodynamics and the limits of flammability of gases expected showed that vapor-phase explosions are a definite possibility with the aqua regia system. Reactions of hydrogen with nitrogen oxides, nitrosyl chloride, and chlorine (possible gaseous products) are highly exothermic, and mixtures of the gases are



explosive over wide concentration ranges. Hydrogen could be produced directly from the dissolution of stainless steel or by reaction of sodium (contained in some fuels) with water. The Sulfex process, in which only hydrogen is evolved, will require safe means for disposal of hydrogen. For a discussion of the problems in the disposal of Sulfex-process off-gases, see Sec. III of this Review. A discussion of the safe handling of off-gases during uranium dissolution is also contained in Sec. III.

### *Nuclear Criticality Safety*

A neutron multiplication technique has been developed to indicate the buildup of  $U^{235}$  in radiochemical separations plants. Uranium-235 solutions are frequently processed or stored in vessels that are not critically safe. A nuclear accident can result if the concentration of  $U^{235}$  exceeds safe limits. Such a possibility is normally guarded against by rigorous procedures. Additional protection can be afforded by measuring the  $U^{235}$  concentration of the solutions.

A more direct method is to monitor the approach of the solution to criticality by measuring neutron multiplication. A multiplication monitor would respond to changes both in the geometry and in the  $U^{235}$  concentration, and thus should supply more positive information on criticality than would a monitor that measures only uranium concentration. The monitor consists of a neutron source (plutonium-beryllium) located in or near the vessel, and a neutron detector (boron trifluoride counter) that measures the neutron leakage from the vessel. The magnitude of the neutron leakage increases with increasing neutron multiplication within the vessel.

Small changes in the  $U^{235}$  content of a 16.5- by 16.5- by 11-in. stainless-steel vessel were readily detected by means of neutron multiplication. A change of 1.0 g/liter in the  $U^{235}$  concentration produced a 5 per cent change in the count rate for solution concentrations between 0.5 and 12.0 g/liter. Similar changes in the count rate were observed when the amount of  $U^{235}$  present was varied by changing the volume of the solution.

The neutron multiplication experiments indicated that a multiplication monitor should furnish adequate warning of a dangerous buildup of  $U^{235}$  in chemical solutions. The monitor is not an acceptable device for process control (e.g., concentration measurements). However, the monitor adequately fulfilled the requirement of indicating a change in neutron multiplication at solution concentrations and geometries that were far from critical.<sup>5</sup>

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## Section

### III

## PREPARATION FOR FUEL PROCESSING

The large number of proposed reactor designs involve a wide variety of fuel types. Before actual processing begins, most fuels require storage, mechanical or chemical disassembly of the element, dissolution of the fuel proper, and perhaps a chemical pretreatment prior to processing.

### *Storage*

Storage of an irradiated fuel element may be required prior to processing in order to reduce activity levels to a point tolerable in the process. This is generally true of solvent-extraction plants.

Storage of nuclear fuel elements was discussed by Rometsch at a recent meeting in Kjeller, Norway.<sup>1</sup> Methods of unloading containers are given, and storage facilities at ORNL and Hanford are described. At ORNL the fuel elements are placed under water in a long storage canal with transverse storing racks built in such a way that no critical arrangement of fuel elements may be produced accidentally. Each rack accommodates just one line of fuel-element buckets. Water compartments 30 cm wide are located between the racks. In addition, an electrical interlocking system of the bridge crane transporting the buckets avoids accidental critical arrangements during transfer of the buckets.

A unique system for storage of fuel elements has been proposed by Hanford for nonproduction fuels. In this system the fuel elements are grouped in a series of storage tanks which in turn are placed in a series of concrete cells. The tanks are filled with water and fitted with cooling coils. Solid neutron absorbers are built in, and, in addition, it is possible to use boric acid as a neutron absorber in the tank water.

### *Mechanical Processing*

For many of the proposed fuels, it would be desirable to remove the decladding material mechanically. Studies at Hanford on mechanical processing of nonproduction reactor fuel elements have been completed, and a terminal report has been issued.<sup>2</sup>

At ORNL further tests are being made in the Sodium Reactor Experiment (SRE) fuel-decladding facility discussed in previous Reviews.<sup>3-6</sup> The fuel elements are comprised of uranium rods in stainless-steel NaK-bonded tubes. Initial tests<sup>7,8</sup> to determine the feasibility of using a spiral inclined rotary drum as a feeder for the leacher indicate some back-mixing of solids when the feeder is operated at an angle of 20 to 30° from the horizontal. The rate of discharge of four 3-liter batches of solid steel rods ( $\frac{1}{2}$  in. in diameter by 1 in. in length) was determined as a function of inclination of the drum.

A material balance flow sheet was calculated for the nitric acid leaching of uranium dioxide from 1-in.-long pieces of stainless-steel-clad uranium dioxide in a 10-stage countercurrent inclined-drum rotary leacher (four leaching and six washing stages). In steady-state operation of a shear-and-leach plant operating on typical tubular fuel bundles, minimizing water and acid usage and using air for oxidation of nitric oxide (NO) to nitrogen dioxide to increase acid recovery, the main product overflow averaged 2M uranyl nitrate-2M nitric acid (at 25°C) before mixing with wash water streams.

To simulate continuous leaching, 18.9 ml of 7M nitric acid per minute was passed for 4 hr over several beds in series, each containing 600 g of Shippingport Pressurized-Water Reactor (PWR) reject uranium dioxide pellets.<sup>8</sup> Steady-state conditions were approached in five

to six stages, and the product composition profile varied from a maximum uranium loading of 550 g/liter and 0.8M acid to 450 g of uranium per liter and 2.0M acid.

### *Chemical Dejacketing*

Selective chemical dissolution of fuel jackets and structural components is an attractive alternate to mechanical dejacketing or complete dissolution. The fuel cores thus exposed can be dissolved by another reagent in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel.

#### **Removal of Zirconium and Zircaloy Jackets**

Oxide-core fuel elements clad with zirconium or Zircaloy may be dejacketed by dissolving the cladding in boiling 5M to 6M ammonium fluoride–0.5M to 1.0M ammonium nitrate solution (Zirflex process). Dissolution may also be accomplished by nitric acid–hydrofluoric acid mixtures. Electrolytic dissolution of Zircaloy in 8M sodium nitrate has also been studied at ICPP.<sup>9</sup>

The Zirflex process is applicable to the processing of fuels from the Dresden and PWR reactors, as well as to Hanford's New Production Reactor (NPR) and Plutonium Recycle Test Reactor (PRTR) fuels. Other possible applications are fuels from the Experimental Breeder Reactor (EBR-I), the Canadian NPD-2 reactor, and the Carolinas-Virginia Nuclear Power Associates reactor. A terminal report on Hanford's development work on the Zirflex process has been issued.<sup>10</sup> Average dissolution rates on unoxidized Zircaloy are 10 to 15 mils/hr at a mole ratio of fluorine to zirconium of 7. Zircaloy, oxidized by exposure to high-temperature air or water, dissolves only 20 to 30 per cent as rapidly as the unoxidized cladding because a pitting and undercutting attack is necessary to penetrate the highly resistant oxide film, which is not soluble in Zirflex solution.

During the Zirflex reaction, hydrogen and ammonia are produced at rates of about 0.1 mole and 5.0 moles, respectively, per mole of zirconium dissolved. Optimum dissolution rates and zirconium solubility require the removal of ammonia from the solution. The ammonia can be effectively removed by steam sparging or rapid boiling without reflux. Air or steam dilution of the off-gases to <4 per cent hydrogen and

<16 per cent ammonia in dry air is required to avoid explosive mixtures. Uranium, uranium–aluminum alloy, and uranium dioxide cores are not severely attacked by the Zirflex solution. Zirflex dejacketing wastes, raised to a pH of 10 with sodium hydroxide, may be safely stored in mild-steel tanks. Although 20 to 30 vol.% solids are generated during the neutralization, the solids can be slurried, and the resulting slurry can be easily transferred by pump or jet.

An acidic fluoride dissolution system that would preferentially remove Zircaloy cladding from uranium or uranium dioxide fuels would avoid the problem of ammonia removal associated with the Zirflex process.<sup>11</sup>

Satisfactory Zircaloy dissolution rates, relatively low container corrosion rates, and low loss of uranium dioxide to the decladding solution may be obtained with a decladding solution containing 2M hydrofluoric acid and a low concentration of nitric acid (0.25M). The nitric acid addition (made to dissolve tin present in Zircaloys) may be made subsequent to decladding. The latter technique is preferable from the corrosion standpoint. The heat of dissolution is sufficient to maintain a high Zircaloy dissolution rate. No applied heat is necessary or desirable.

At ICPP two tests were made in which Zircaloy was disintegrated electrolytically in 8M sodium nitrate.<sup>10</sup> It was found that, apparently unlike the case with nitric acid, this reaction is favored by higher temperatures of the order of 110°C. If uranium–Zircaloy-2 alloy is treated in this manner, essentially none of the uranium is dissolved. The final solution is slightly basic. The cathodic potential is too large to measure with the present equipment, and the corrosion rate of stainless steel is too small to measure in a 2-hr test, in contrast to acid solutions where the corrosion is excessive. Partial removal of the uranium from the zirconium oxide precipitate was effected by digestion in 2M nitric acid.

#### **Removal of Stainless-Steel Jackets**

Stainless-steel jackets may be removed by the Sulfex process, in which boiling 3M to 4M sulfuric acid is used to dissolve the stainless-steel fuel-element cladding. Dissolution rates vary with the type of stainless steel and with the type of gas sparge; sparging with superheated steam rather than air gives improved dissolu-

tion rates. At 25°C, approximately 50 to 80 g of stainless steel per liter will form stable solutions in sulfuric acid concentrations<sup>2</sup> of 2M to 5M. However, the solubility decreases rapidly as the sulfuric acid concentration increases until, in a liter of 8M sulfuric acid, only 10 g of stainless steel will remain in solution. Passivation of stainless steel to boiling 3M to 4M sulfuric acid is no problem if the nitrate ion concentration is below 0.01M and the fuel elements are coupled to carbon steel. Uranium losses to the decladding solutions are approximately 0.25 per cent. The hydrogen evolved during the dissolution must be diluted with air, steam, or inert gas to give a nonexplosive mixture. The cladding wastes from the Sulfex process can be neutralized with sodium hydroxide and jetted or pumped to mild-steel tanks for safe storage.

Chemical decanning and dissolution have also been discussed by Hultgren.<sup>12</sup> The main factors governing the choice of cladding and core dissolution procedures were outlined as follows:

1. A rapid chemical attack compatible with reaction control and a reasonable time of dissolution
2. A waste solution stability compatible with as small volume as possible for the decladding waste solution
3. A minimum of uranium and plutonium losses in the decladding waste solution. Plutonium concentrations are higher in the surface layer of the fuel core because of neutron spectrum change and absorption cross-section dependence on neutron energy for  $U^{238}$ , and plutonium losses are thus usually higher than the losses of uranium
4. Corrosion rate of the dissolver for the different reagents used

## Dissolution

Some chemical processes discussed in this section are designed for simultaneous dissolution of the jacket and core, and others are designed for dissolution of dejacketed material. For zirconium alloy fuels, the processes being investigated include nitric acid-hydrofluoric acid dissolution, a modified Zirflex process, and the Alloy Reguline Chloride Oxidation (ARCO) (fused lead chloride) process. Processes for dissolution of dejacketed fuels are discussed for uranium carbide fuels, uranium dioxide-beryllium oxide fuels, and Submarine

Thermal Reactor (STR) fuel. Uranium carbide fuels may be dissolved in 90 per cent nitric acid or by an electrolytic process. For dissolution of uranium dioxide-beryllium oxide fuels, leaching in boiling 6M to 13M nitric acid recovers the uranium and leaves an undissolved beryllium oxide residue. The uranium dioxide-beryllium oxide pellets may be completely dissolved in boiling 8M nitric acid-0.2M sodium fluoride. Uranium dioxide-beryllium oxide pellets may also be dissolved in dilute aqua regia mixtures.

## Combined Dissolution of Jacket and Core

*Behavior of Niobium in the ARCO Process.* The ARCO fused-salt process under development at ICPP<sup>3-6</sup> continues to look promising for head-end treatment of zirconium-uranium fuel alloys and dissolution of other alloys. This process employs molten lead chloride as a solvent for zirconium-uranium alloys, and lead chloride is then regenerated from the lead produced. The effect of using other cladding materials, such as niobium, is being examined.

In furtherance of the investigation of niobium behavior in ARCO systems, the rates of dissolution of niobium were measured in lead chloride-chlorine melts<sup>10</sup> at 550°C. The increase in dissolution rate appears to be linear with chlorine flow rates from 3 to 10 mg/min. Typical results for a 30-min contact period were 1.4 mg/(cm<sup>2</sup>)(min) at 3.3 mg of chlorine per minute and 2.4 mg/(cm<sup>2</sup>)(min) at 9.6 mg of chlorine per minute. Niobium dissolution rates of up to 6.4 mg/(cm<sup>2</sup>)(min) were measured at 550°C and 53 mg of chlorine per minute. Experiments concerned with niobium dissolution behavior in the ARCO system have shown that >99 per cent of the niobium volatilizes from lead chloride-chlorine melts.<sup>13</sup> Studies are under way to determine the niobium chloride species in the sublimate.

*Electrolytic Dissolution of Zircaloy-Clad Uranium Dioxide Fuel.* In studies of electrolytic dissolution in boiling 10M nitric acid at Savannah River,<sup>14</sup> half of a charge of 15 unirradiated PWR blanket rods, consisting of uranium dioxide clad with Zircaloy-2, was disintegrated in 7 hr in the semiworks dissolver. An average alternating current of 65 amp was used at a constant potential of about 19 volts. The uranium loss to the sludge was not significant (<0.1 per cent).



*Dissolution of Stainless-Steel-Clad Fuel Elements.* A proposed method for dissolution of stainless-steel-clad uranium or uranium dioxide is electrolytic dissolution in nitric acid. In studies at Savannah River,<sup>15</sup> more than 99 per cent of the uranium was dissolved during the electrolytic dissolution of a stainless steel-uranium dioxide cermet fuel element in 4M to 10M nitric acid. About 6 per cent of the element disintegrated to form a sludge containing 0.4 per cent uranium. Half of the uranium in the sludge was dissolved by leaching with boiling nitric acid.

*Zircex Process for TRIGA Fuel.* A Zircex process was developed at ORNL<sup>8</sup> for recovering uranium from spent TRIGA reactor fuel. The aluminum cladding, the aluminum-samarium burnable poison, and the core of 8 per cent uranium-92 per cent zirconium hydride are hydrochlorinated at 300 to 600°C to produce volatile aluminum and zirconium chloride and relatively nonvolatile uranium chloride containing some oxide impurities. The residual uranium trichloride and oxide impurities are converted to volatile chlorides by chlorination with carbon tetrachloride vapor at 550°C. The volatilized uranium chloride is selectively condensed at 300°C, and the zirconium and aluminum chlorides are condensed downstream at room temperature. The condensed uranium chlorides are dissolved in nitric acid prior to chloride removal and solvent extraction. The entire process requires 22 hr. The off-gas is hydrogen and carbon dioxide.

*Composition and Safe Handling of Off-Gases from Uranium Dissolutions.* During dissolution of claddings and cores of uranium fuel elements, halogens, hydrogen, and rare gases are evolved. Iodine-131 is a fission product of particular concern in dissolution of irradiated uranium since over half the iodine in the irradiated uranium is evolved with the off-gas during a nitric acid dissolution.

A simplified flow diagram showing the source and disposition of airborne fission-product activity at the Hanford Purex plant<sup>16</sup> is presented in Fig. III-1. Heavy flow lines are used to denote relatively high concentrations of fission products. From the standpoint of gas decontamination, the principal items of process equipment are the silver reactors, the in-canyon off-gas filters, the building-ventilation-exhaust filter, the nitric acid and iodine-recovery facility, and the vacuum nitric acid fractionator.

Much of the process equipment (not shown) within the Purex plant is designed to suppress fission-product volatilization and entrainment. The flow of I<sup>131</sup> is, in general, similar to that of other fission products shown in Fig. III-1, except that the bulk of the released iodine is trapped in the silver reactors rather than in the in-canyon filter. The process vent system, which vents the major Purex vessels, is a major potential source of airborne fission-product particulate material; process vent off-gas passes through two filters in series prior to discharge to the atmosphere. Adequate deentrainment is obtained in vessels of the dissolver off-gas trains such that only a single filtration step is required. Gas discharged from the 200-ft-high Purex stack is monitored continuously for radioiodine and fission-product particulate material.

Hazards in handling off-gas from Sulfex decladding of Plutonium Recycle Fuel Reactor (PRFR) have been outlined by Holmes at ORNL.<sup>17</sup> Removal of rare gas from the PRFR pilot-plant dissolver off-gas will involve certain hazards in addition to those connected with the radioactivity of the gaseous wastes. Part of the hazards will be created by the constituents of the off-gas streams such as the hydrogen generated by Sulfex decladding, whereas others will be determined by the rare-gas removal process, such as the buildup of liquid oxygen in the rectification column during liquid-nitrogen scrubbing.

Hydrogen will be evolved during the Sulfex decladding operation at rates up to a maximum estimated at 25 scfm. Present plans call for burning of this stream in a submerged combustion system after removal of the rare gases in order to prevent the discharge of hydrogen into the ventilation air sent to the stack. However, this scheme necessitates the flow of hydrogen through the rare-gas removal equipment at alternate periods with gases that may contain oxygen or the oxides of nitrogen. It will also be required that hydrogen be compressed to between 30 and 100 psig if a liquid-nitrogen or Freon absorption process is used. If an adsorption process is specified, compression may not be necessary, but larger diameter beds will be required owing to the higher gas velocities at the lower pressures.

#### Dissolution of Dejacketed Material

Dissolution of the core is possible if fuel jackets can be removed mechanically or chemi-



acid; after two 4-hr leaches, 60 per cent of the  $Ce^{144}$ , 35 per cent of the  $Ru^{106}$ , and 38 per cent of the  $Zr^{95}$  remained in the graphite residue.

In engineering time-cycle tests, graphite-3 per cent uranium fuel leached 24 hr at 60°C or 96 hr at 25°C with 88 to 91 per cent nitric acid contained about 600 ppm undissolved uranium, indicating that extended leaching at lower temperatures may be less effective than several higher temperature acid leach-water wash cycles for the same total processing time.

In laboratory tests the behavior of fission products in the 90 per cent nitric acid process is being determined with slightly irradiated ( $\sim 0.001$  per cent burnup) specimens. When specimens containing 3 and 12 per cent uranium were leached twice for 4 hr at 25°C, both graphite residues retained 38 to 46 per cent of the  $Zr^{95}$ , 28 to 80 per cent of the  $Cs^{137}$ , 46 to 63 per cent of the  $Ru^{106}$ , and about 75 per cent of the  $Ce^{144}$ ; 1.2 per cent of the uranium was lost to the residue from the 3 per cent specimen, and, in the case of the 12 per cent specimen, 0.13 per cent of the uranium was lost to the residue.

In sedimentation tests, only 0.4 per cent of unirradiated graphite-3 per cent uranium fuel exposed to fuming nitric acid for 24 hr at 30 to 80°C was disintegrated to 10- $\mu$  particles. It is thought unlikely that mechanical attrition in subsequent water washes would measurably increase the fraction of <10- $\mu$  particles.

Hydrolysis of uranium monocarbide by water at 80°C yielded principally a finely divided, insoluble uranium compound and 92 ml of gas per gram of uranium monocarbide. The off-gas contained 86 per cent methane, 11 per cent hydrogen, small amounts of ethane and propane, and a trace of ethylene. Hydrolysis of uranium monocarbide specimens containing about 20 per cent uranium dicarbide resulted in the evolution of 77 ml of gas per gram of sample. The off-gas from this sample contained 75 per cent methane, 14 per cent hydrogen, and 8 per cent ethane. The off-gas from the high-purity uranium monocarbide contained 3.8 millimoles of carbon per gram, but only 3.4 millimoles/g was found in the uranium monocarbide-uranium dicarbide mixture even though it contained more carbon per gram. Specimens containing uranium dicarbide yielded some wax. In both experiments the carbon that was not accounted for was probably present as hexane and higher hydrocarbons, which were not detected by the analytical methods used.

In laboratory tests uranium monocarbide reacted with 5.6M hydrochloric acid at 80°C to produce a green solution in which the uranium was >99 per cent tetravalent. The reaction rate was much slower with 5.6M hydrochloric acid than with water. The off-gas contained 91.6 ml (STP) of gas per gram of carbide and consisted of 10 per cent hydrogen, 88 per cent methane, 1 per cent ethane, and small amounts of paraffins with 3 to 7 carbon atoms.

Uranium monocarbide reacted with 4M nitric acid to produce a dark-red solution. Near the end of the reaction, the off-gas was 65 per cent nitric oxide, 23 per cent carbon dioxide, 4 per cent nitrous oxide, 1 per cent carbon monoxide, and 5 per cent nitrogen (probably from atmospheric contaminants), and had a faint brown color indicative of nitrogen dioxide.

An unirradiated fuel element made of graphite-14 per cent uranium was disintegrated electrolytically in boiling 10M nitric acid.<sup>13</sup> Current utilization was 0.75 g/amp-hr at a current density of 0.63 amp/cm<sup>2</sup>. Loss of uranium to the sludge after leaching for 3 hr in boiling 10M nitric acid was about 0.1 per cent of the total uranium.

*Beryllium Oxide Fuel Dissolution.* The fuel for the GCRE (Gas-Cooled Reactor Experiment) is Hastelloy-X-clad 70 per cent uranium dioxide-30 per cent beryllium oxide. In tests at ORNL,<sup>7</sup> leaching of GCRE fuel pellets for 65 hr in boiling 6M to 13M nitric acid recovered 99.9 per cent of the uranium; approximately 50 per cent of the beryllium oxide remained as an undissolved residue. In boiling 8M nitric acid-0.2M sodium fluoride, the pellets dissolved completely in 30 to 40 hr. Uranium dioxide-beryllium oxide pellets containing 66 to 70 per cent uranium dioxide disintegrated to powder when heated in air at red heat. Niobium dissolved at a rate of 5.5 mg/(cm<sup>2</sup>)(min) in 30M potassium hydroxide at 325°C.

Unirradiated GCRE fuel pellets containing 70 per cent uranium dioxide-30 per cent beryllium oxide were completely dissolved in boiling 2M nitric acid-4M hydrochloric acid in 22 hr and in boiling nitric acid-sulfuric acid solutions with molarity ratios of 3 to 5, 3 to 7, 5 to 3, and 7 to 3 in about 24 hr.

When unirradiated Maritime Gas-Cooled Reactor (MGCR) prototype uranium dioxide-8 per cent aluminum oxide and uranium dioxide-13.5 per cent aluminum oxide fuel pellets were

leached with boiling 10M nitric acid for 4 hr, uranium losses to the undissolved aluminum oxide residue were 1.3 and 3.3 per cent, respectively.

Study of the grind-leach flow sheet for recovering uranium from beryllia-containing ceramic fuels at ICPP has shown<sup>10</sup> that successive nitric acid leaches of a fuel sample gave little or no increase in the over-all recovery of uranium.

Preliminary results obtained from the sulfuric acid dissolution of ceramic fuel pieces agree closely with predicted flow-sheet conditions, indicating that a flow sheet similar to that for stainless-steel fuel processing may be feasible.

*Modified Zirflex Process for TRIGA Fuel.* A modified Zirflex process compatible with stainless-steel equipment was developed at ORNL<sup>7</sup> for recovering uranium from spent TRIGA reactor fuel (aluminum-clad 8 per cent uranium-91 per cent zirconium-1 per cent hydrogen). The cladding and the aluminum-samarium burnable-poison disks are first dissolved in sodium hydroxide-sodium nitrate solution. The graphite moderator plugs are then disintegrated with cold mixed acid (90 per cent 21N nitric acid-10 per cent 40N sulfuric acid). The core is then dissolved in 5.4M ammonium fluoride-0.33M ammonium nitrate-hydrogen peroxide, and nitric acid and aluminum nitrate are added to produce a stable solvent-extraction feed containing 0.0085M uranium. The entire process takes 14 hr. The decladding off-gas is ammonia, and the core dissolution off-gas is 10 per cent hydrogen, 0.5 per cent oxygen, 2 per cent nitrogen, and 87 per cent ammonia.

*Modified STR Dissolution Process.* The modified STR dissolution process<sup>18</sup> being developed at ICPP is designed to dissolve low uranium-zirconium alloys (up to 3 per cent uranium) in 10M hydrofluoric acid solution that has been made 0.06M in hydrogen peroxide. The existing process is designed for a maximum of 1 per cent uranium. The modified batch flow sheet is compared with the existing STR flow sheet in Table III-1. Continuous flow sheets have also been suggested.

The potential advantages of these flow sheets, as compared to the currently used flow sheets, are (1) the STR hydrofluoric acid process can be adapted to handle up to 3 per cent uranium fuels, (2) the uranium throughput of a given ex-

Table III-1 COMPARISON  
OF STR BATCH FLOW SHEETS<sup>18</sup>

	Existing	Modified
Uranium in fuel, %	1 or less	3 or less
Dissolution reagent	10M HF	10M HF
Oxidation of U in dissolver	0.016M HNO <sub>3</sub>	0.06M H <sub>2</sub> O <sub>2</sub>
Moles of ZrO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> per kilogram of U	900	750

traction system can be increased by as much as 20 per cent by using the more concentrated extraction feed, and (3) the more concentrated stored waste can be obtained without the corrosion and stability problems associated with evaporation.

## Pretreatment of Dissolver

### Solution: Removal of Silica from Darex Dissolver Solution

The silica present in the Darex dissolver solution after dissolution of stainless-steel-clad fuels must be removed to prevent formation of emulsions at the organic interface in the subsequent solvent-extraction process.

The most effective method of silica removal from Darex dissolver solutions and the one that shows the most promise combines a fluoride and gelatin treatment.<sup>19</sup> A 15-min digestion at 95 to 100°C with 0.01M fluoride, followed by cooling to 80°C and addition of 0.15 g of gelatin per liter, resulted in complete and immediate separation of silica from solution in a form that was removed on a 30- to 70-mesh graded sand filter.

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## Section IV

## RESEARCH AND DEVELOPMENT ON FUEL PROCESSING

### Solvent Extraction

An excellent review of aqueous processing both past and present is provided in the compilation of lectures presented during the summer of 1960 at the Netherlands-Norwegian Reactor School. The established processes, Purex, Redox, and Butex, are covered adequately, and mention is made of a Russian process using dibutyl ether. A special section is devoted to the more recent applications of tributyl phosphate (TBP) processing. A section on organonitrogen extractants provides an abundance of well-cataloged information on systems that are adaptable to various fuel-processing problems.<sup>1</sup>

### Development in Purex Processing

Purex processing (TBP extractant) is well established in production facilities, as shown by the list of TBP processing facilities provided in reference 1. The need remains, however, to adapt the process to some of the atypical nonproduction reactor fuels and to obtain detailed data on the extraction power of TBP under various conditions.

In studies at the Savannah River Laboratory (SRL)<sup>2</sup> unirradiated zirconium-uranium fuel plate was dissolved in nitric acid-hydrofluoric acid and adjusted with aluminum nitrate to provide a feed solution of the composition shown in Table IV-1. The aluminum nitrate provides a salting agent and also reduces corrosion problems by complexing excess fluoride ion. The concentration of aluminum nitrate was found to be critical. Too low a concentration failed to complex fluoride, and too high a concentration caused the precipitation of zirconium tetrafluoride. Tests of the process in a miniature mixer-settler showed good recovery of uranium, but, unexpectedly, precipitates were ob-

Table IV-1 TWO-CYCLE SAVANNAH RIVER FLOW SHEET FOR THE RECOVERY OF URANIUM FROM ZIRCONIUM-URANIUM FUEL<sup>2</sup>

Stream	Flow rate	Composition
<i>First Cycle</i>		
Feed	100	0.5M Al <sup>3+</sup> , 0.4M Zr <sup>4+</sup> , 2.0M F <sup>-</sup> , 0.025M H <sub>2</sub> CrO <sub>4</sub> , 0.7 g of U per liter
Extractant	250	7.5% TBP in Ultrasene
Scrub	50	0.8M Al(NO <sub>3</sub> ) <sub>3</sub> , 0.04M ferrous sulfamate
<i>Second Cycle</i>		
Strip	50	0.02M HNO <sub>3</sub>

served in the feed and scrub stages of the first cycle. The precipitate in the scrub stage contained small amounts of chromium and was believed to result from extraction of chromic acid by the organic phase with subsequent degradation of TBP. Chromic acid was added to the feed to oxidize U(IV) to U(VI). Subsequent batch tests indicated that destruction of the excess chromic acid with sodium nitrite prevents formation of the precipitate.

The Purex process achieves relatively poor ruthenium decontamination because of nitrosyl ruthenium nitrate complexes that strongly favor the organic phase. Preliminary studies indicate that significant improvement in ruthenium decontamination may be achieved by treatment of the first-cycle uranium product with hydrazine nitrate. Batch studies<sup>3</sup> showed that adjustment to 0.1M NH<sub>2</sub>NH<sub>2</sub> and digestion at 70°C for 1 hr reduced the ruthenium distribution coefficient,  $E_a^o$ , from 0.025 to 0.007.

Relatively few uranium and nitric acid distribution data have been reported for Purex systems at temperatures in excess of 25°C.

A report presenting calculated data for temperatures to 70°C is now available.<sup>4</sup> Based on the assumption that the uranium complex in the organic phase contains 1 mole of uranyl nitrate and 2 moles of TBP, thermodynamic considerations were employed to calculate the equilibrium distribution of uranium and nitric acid at temperatures above 25°C. Tables are provided giving equilibrium data for uranium concentrations from zero to 0.5M and nitric acid concentrations from zero to 0.3M in temperature increments of 5°C between 25 and 70°C.

Complete distribution data, obtained by contacting nitric acid with pure dry TBP at 25°C, have been reported. These data are shown in Fig. IV-1. Diligent efforts were made to de-

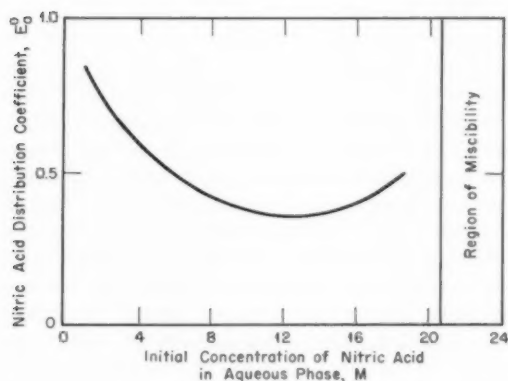


Fig. IV-1 Distribution of nitric acid between TBP and water.<sup>5</sup>

termine the composition of the extracted complex by spectroscopic, infrared, and proton magnetic resonance measurements.<sup>5</sup>

A somewhat unusual approach to the estimation of the number of theoretical stages by graphical solution of the McCabe-Thiele diagram is presented in a recent report. The problem involved the separation of small quantities of uranium from macrothorium. In the process thorium is stripped in a two-section or compound cascade. To achieve a solution, it was necessary to have prior knowledge of the number of stages in one section of the cascade. The graphical solution was accomplished by first constructing the thorium diagram and using this to estimate the equilibrium uranium concentration in each stage. By a trial-and-error process, several operable flow sheets were developed. Data subsequently ob-

tained in batch countercurrent equipment verified the calculated flow sheets.<sup>6</sup>

### Studies of Alternate Extractants

There now exists a growing body of data showing that, for many processing requirements, several organonitrogen and organophosphorus compounds offer advantages over TBP. Such an extractant is di-2-amyl-2-butyl phosphonate (DABP). Distribution data for trace concentrations of uranium, plutonium, and zirconium are presented in Fig. IV-2. In a series

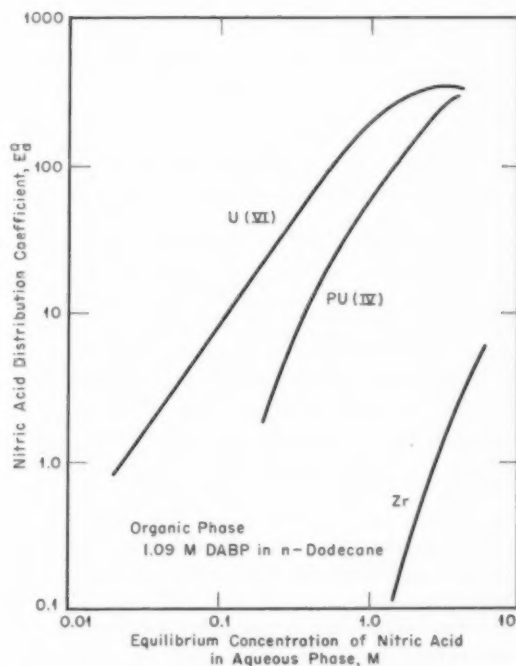


Fig. IV-2 Extraction of tracer U(VI), Pu(IV), and zirconium with DABP.<sup>7</sup>

of batch tests, it was determined that DABP does not form a third phase in dodecane diluent, as is the case for most of the other organophosphorus extractants of recent interest. An attribute of DABP is its superior resistance to chemical degradation. The prior contacting of 1M DABP with 3M nitric acid for 1 hr had no effect on the zirconium distribution coefficient. By comparison, TBP would extract 20 per cent more zirconium after the aforementioned chemical degradation because of the formation of dibutyl phosphate (DBP).<sup>7</sup>

An attractive replacement for TBP in the Purex process is di-*sec*-butylphenyl phosphonate (D-S-BPP). With respect to diluents, Solvesso-100, an aromatic compound, is superior to kerosene as a solvent for the uranium-extractant complex and in its ability to resist radiation damage. A comparison of uranium to mixed-fission-product separation factors for D-S-BPP in Solvesso-100, TBP in Solvesso-100, and TBP in Amsco is presented in Fig. IV-3. D-S-BPP in Solvesso-100 was signifi-

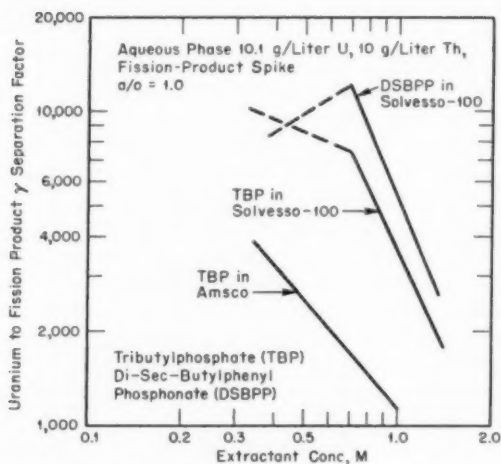


Fig. IV-3 Comparison of gross gamma separation factors for various extractants.<sup>8</sup>

cantly superior to TBP in Solvesso-100. The most interesting finding was, however, that both D-S-BPP in Solvesso-100 and TBP in Solvesso-100 were markedly superior to TBP in Amsco.<sup>8</sup>

Studies of the direct precipitation of uranium as ammonium uranyl tricarbonate (AUT) from extractants continue. This rather drastic approach is occasioned by difficulties in stripping uranium from many of the alternate extractants. Alkyl phosphoric acids, for example, are prone to precipitate as their sodium salts when contacted by basic stripping solutions.

The direct precipitation of AUT has been demonstrated in a 51-hr run in bench-scale mixer-settlers. The extractant, 0.06M Alamine 336 (trialkylamine) modified with 2 vol.% tri-decanol, was loaded by contacting with sulfuric acid ore leach liquor. Repeated recycle of the ammonium carbonate stripping solution results in the buildup of ammonium sulfate. The ura-

nium solubility decreases as the ammonium sulfate concentration increases. In batch studies it was established that, in a stripping solution maintained at an ammonium carbonate concentration of 0.5M, the uranium concentration decreased from 4.5 to 1 g/liter as the ammonium sulfate concentration increased from 0.5M to 2M. As AUT precipitates, it is removed continuously by filtration, washed with sodium hydroxide, and calcined to  $U_3O_8$  at 500°C. In the demonstration run, stripping, precipitation, and filtration were accomplished satisfactorily at 40°C. The calcined product<sup>9</sup> was adequately decontaminated and assayed 99 per cent as  $U_3O_8$ .

Amines are notably well suited to the recovery of plutonium from nitric or sulfuric acid solutions. Typical applications would be, in the case of production reactor fuels, the further decontamination of the first-cycle plutonium product or in the primary decontamination cycle for plutonium-rich fuels. A survey of a number of amines showed greater extraction power from nitrate solution for quaternary and tertiary amines than for secondary and primary amines.<sup>10</sup> The converse was true in the case of sulfate solutions. Plutonium extractability, in both nitrate and sulfate solutions, in decreasing order of oxidation states was IV > VI > III. Extractions by phosphates and phosphonates were similar to TBP extractions. In most cases sodium carbonate was the most effective stripping agent. A very useful section of this report is an excellent reagent list identifying a large number of amines and organophosphorus compounds by trade name and structure.<sup>10</sup>

In a test of an alternate flow sheet for the separation of transplutonium and rare-earth elements by liquid-liquid extraction, the mixed elements were extracted from nitrate solution with TBP, scrubbed with 12N lithium chloride to remove nitrate, and stripped with 7N lithium chloride.<sup>11</sup> The stripping solution was adjusted to 8N lithium chloride and 2N aluminum chloride and fed to a multistage partitioning contactor. An americium-europium separation factor of 10 was realized by extraction with 0.5M tertiary amine in aliphatic hydrocarbon diluent scrubbed with 8N lithium chloride-2N aluminum chloride. This procedure does not appear to be superior to the mono-2-ethylhexyl phosphoric acid process mentioned in the previous Review.<sup>12</sup>

Improved actinide-lanthanide separation is provided by tri(iso-octyl)amine (TIOA). Mixed elements were extracted from 11M lithium chloride with 30 per cent TIOA in 10 per cent iso-octyl alcohol-Amsco.<sup>13</sup> The order of extractability was californium > americium > curium. The californium-americium separation factor was about 20. Lanthanide extractability increased from lanthanum to europium and then decreased to lutetium. The americium-europium separation factor was about 100. A test of the flow sheet<sup>13</sup> using seven scrub and seven extraction stages gave 99.9 per cent recovery of americium with decontamination from macro rare earths by a factor of 10,000.

### Solvent Degradation

Process solvents are susceptible to both chemical and radiation damage. Some of the degradation products are objectionable because they adversely affect uranium recovery, fission-product decontamination, or contactor performance. The search for extractants and diluents highly resistant to degradation is being urgently pursued in preparation for the higher burnups and complex chemical environments associated with the processing of nonproduction reactor fuels. It is now apparent that the proper selection of the Purex diluent can contribute much to the moderation of the problem of solvent degradation. Diluent degradation products, especially nitroparaffin reaction products, form strong complexes with zirconium and ruthenium which are not completely removed by the usual solvent cleanup procedures. Kerosene, the diluent most frequently employed in the Purex process, is now known to be a rather poor choice from the standpoint of its ability to resist degradation.

Comparison of the chemical degradation of various diluents is provided in a British report.<sup>14</sup> The diluents studied include: odorless kerosene (Shell), *n*-dodecane, Shellsol T, hydrogenated propylene Tetramer, and Mepasin. Degraded solvents, consisting of 20 per cent TBP in the selected diluent, were prepared by agitation with equal volumes of an aqueous phase containing 1M to 4M nitric acid, zero to 0.1M in sodium nitrite, and, in some experiments, 54 g of uranium per liter. Odorless kerosene (OK), after an induction period of 40 hr, showed a linear increase in degradation during the course of the 140-hr experiment.

Significantly, with nitrite present, no induction period was observed. However, sulfamic acid is apparently a nitrite inhibitor inasmuch as in its presence no degradation was observed after contacting with 4M nitric acid for 70 hr at 70°C. The alternate diluents were degraded by contacting with 4M nitric acid for 20 hr at 70°C. Neither nitrite nor uranium was added. The results showed *n*-dodecane to be 100 times more stable than kerosene. The other diluents tested<sup>14</sup> were more stable than kerosene by factors of 5 to 23.

Concurrent with the search for alternate diluents, various techniques for the regeneration of degraded solvent are being studied. The most recently published Oak Ridge studies<sup>8</sup> employed 1M TBP in Amsco degraded by Co<sup>60</sup> irradiation to 45 watt-hr/liter in the presence of nitric acid. The degree of degradation was measured by the zirconium-niobium extraction power of the solvent. The standard procedure of washing with 0.2M sodium carbonate was used to eliminate easily removed degradation products. The resultant solvent was then used to determine the efficacy of various adsorbents. The most successful treatment employed manganese dioxide. Fifty to 60 per cent of the degradation products were easily removed; another 20 to 25 per cent were removed with difficulty or were not removed. The treatment, referred to as the alkaline permanganate treatment, involves the use of potassium permanganate dissolved in sodium carbonate solution. The manganese dioxide formed sorbs the solvent impurities. Alumina at 2 to 200 g/liter was also studied, but it was found that 20 times more alumina was required to accomplish the same job.<sup>8</sup>

The British studies,<sup>14</sup> using solvents degraded chemically, are in essential agreement with the Oak Ridge results. Again the solvent cleanup techniques were evaluated in terms of the ability of the solvent to retain selected fission products; namely, Zr<sup>95</sup>, Ru<sup>106</sup>, and Hf<sup>181</sup>. Alkaline washes were found to remove most of the fission-product activity, but the complexes themselves were not affected and remained in the solvent as their sodium salts. Solid adsorbents were of little value except in the case of strong oxidizing agents, i.e., permanganate.<sup>14</sup>

From the standpoint of plant operation, the entrainment of aqueous phase or solid material in the solvent is a major source of impurities. The use of an electrostatic precipitator has been demonstrated to be an effective method of



coalescing finely dispersed particles.<sup>15</sup> This technique is effective when the dispersed phase conducts an electric current and the continuous phase is only slightly conductive. In tests of a plant-scale precipitator, consisting of a high d-c voltage gradient electrode with alternate grounded and charged concentric cylinders, up to 10 per cent aqueous entrainment could be reduced to <0.05 per cent. In-plant studies showed that the average extractant entrainment of 0.2 per cent was reduced to 0.003 per cent by the electrostatic precipitator.<sup>15</sup>

In a fundamental study of the effect of ionizing radiation on organophosphorus compounds, data were obtained on the homologous series of tri-*n*-alkyl phosphates from trimethyl to tri-pentyl.<sup>16</sup> The study employed 1.25-Mev electrons produced by a Van de Graaff accelerator. Tables and graphs showing the yields of various degradation products are presented, and various mechanisms for the formation of acid alkyl phosphates and other degradation products are considered. Generalizing, the electron irradiation of trialkyl phosphates leads to the formation of the corresponding dialkyl phosphate as the major product, the absolute yield decreasing in the series trimethyl to tri-pentyl phosphate.

### Fundamental Studies

A topical report is available describing a novel procedure for estimating the resistance to mass transfer across an interface in the water-uranium-TBP system.<sup>17</sup> Observations were made of a steady-state concentration gradient across an interface in terms of a molecular flux defined as the product of diffusivity and concentration gradient. Evidence of an interfacial resistance was indicated by a departure from equilibrium concentrations at the interface. Accurate point analyses were obtained without sampling by a light transmission technique. A steady-state profile and a molecular flux were established in a specially designed 2-mm-square by 12-mm-long column. The organic phase, 30 per cent TBP in Amsco, was maintained uranium free. The aqueous phase at the bottom of the column was maintained at saturation by the presence of uranyl nitrate crystals. By the use of photographs to measure transmitted light, it was possible to measure concentration profiles to within 100  $\mu$  of the interface. Extrapolation of the steady-state profile to the interface showed the two phases

to be at equilibrium. From this it was inferred that the system offers no interfacial resistance to mass transfer.<sup>17</sup>

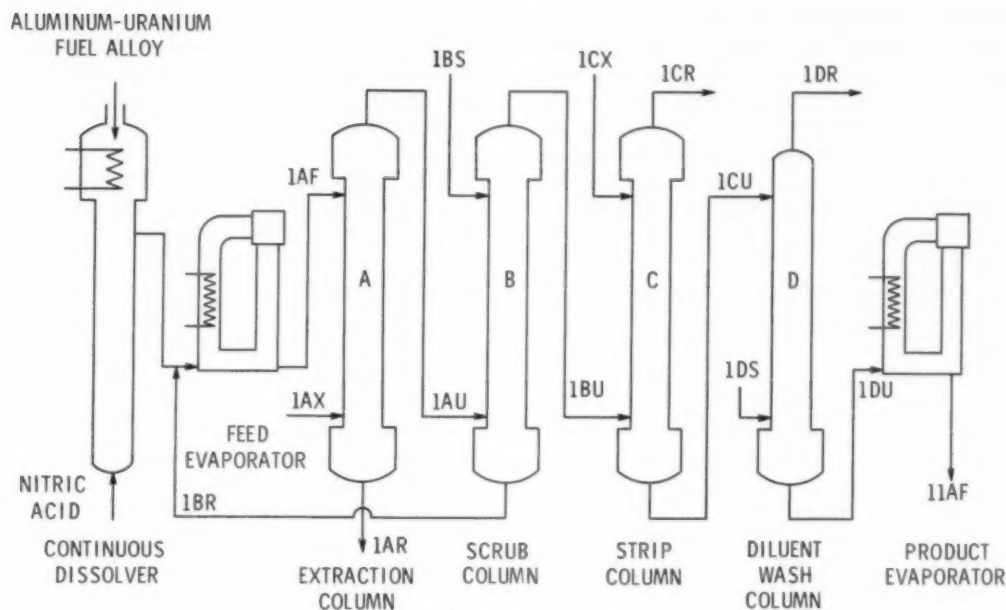
Studies of a technique for measuring interfacial area between an aqueous solution of an alpha emitter and an organic phase containing a liquid scintillator have met with some success. Short-range alpha particles activate the scintillator to within a few microns of the interface, and the light produced is detected by a photomultiplier. In the system studied, uranyl ion (100 g/liter) provided the alpha source, and transstilbene (5 g/liter in phenyl cyclohexane) provided the scintillator. Equations are presented relating the interfacial area, alpha energies, and various instrument parameters.<sup>18</sup>

In another study of emulsions of immiscible liquids, the variation of mean drop size in a stirred tank as a function of distance from the impeller was determined. As expected, the drops were observed to be smallest at the tip of the impeller and largest at the top and bottom of the vessel. A correlation was developed relating mean drop diameter at any point to an equilibrium drop diameter, a coalescence term, the physical properties of the system, and the Weber and Reynolds numbers.<sup>19</sup>

### Plant and Equipment Design,

#### Development, and Operation

A recently declassified document<sup>20</sup> makes available much of the experimental, plant assistance, and process evaluation experience from work with the Chemical Plant Modification (CPM) in Idaho during the 1955-1956 period of startup and processing. The CPM, a head-end system that was added to the existing plant facilities, consists of a continuous dissolver, one-cycle TBP solvent-extraction system, solvent wash system, and aqueous waste concentration facilities. The modification was designed to provide the ICPP with an improved facility for processing enriched uranium-aluminum alloy fuel. The facility also provides a plant-scale test of two major innovations: the operation of continuous dissolvers and the dual solvent-extraction chain (one TBP cycle and two hexone cycles). The design flow sheet provided for the daily processing of the uranium associated with 370 kg of aluminum. Since the diluent metal (i.e., aluminum cladding or structural pieces) actually determines the limit-



ing processing rate, the uranium rate varies with fuel composition and burnup.

A schematic representation of the facility first cycle is given in Fig. IV-4. Enriched uranium-aluminum alloy fuels are charged semicontinuously to the top of the dissolvers, whereas acid and catalyst (which are metered separately) are pumped in the bottom of the dissolvers. Operation is thus countercurrent with the full slug bed submerged in acid or foam. Product overflows at the top of the slug pack, and the vapors are condensed and returned to the dissolver feed stream. The density of the flowing stream of dissolver product is recorded continuously, and this record is used to indicate the need for minor changes in the dissolution rate, which are effected by changing the catalyst injection rate. The dissolver product is accumulated by either of two collection tanks where the batch density, acidity, uranium concentration, and volume are determined. From these tanks the feed is jetted to the feed tank, from which it is metered into the head-end evaporator. In this head-end evaporator, the scrub column raffinate (IBR) is blended with the fresh feed, and these streams are concentrated to column feed (IAF) specifications.

The three major columns in the cycle are pulsed sieve-plate columns.<sup>20a</sup> A simple extraction column is used with 4½ per cent TBP (tri-*n*-butyl phosphate) in Amsco 125-90W solvent. The remaining two pulse columns are for scrubbing the organic extract and for stripping the uranium into dilute nitric acid. A packed column is provided for washing the strip-column product with Amsco diluent for the removal of traces of TBP from the product prior to evaporation. A steam stripper (not shown in Fig. IV-4) between D column and the product evaporator is also provided for the removal of TBP and other organics. The uranium-bearing strip solution is concentrated in the first-cycle product evaporator to make feed for the second cycle. The strip-column organic raffinate, ICR, is washed in three successive mixer-settlers with dilute nitric acid, sodium carbonate solution, and dilute acid. The recovered solvent is recycled. The first-cycle aqueous raffinate, IAR, and the spent washes from the first two solvent wash mixer-settlers are concentrated together continuously and then transferred to permanent storage.

The results of the plant study concerning the design flow sheet and flow-sheet modification,

effects of acid feed rate, catalyst concentration and feed burnup on the dissolution rate, process engineering performance of the extraction columns, and evaporator operation are given in considerable detail. No attempt to summarize these results will be made here except to note some points of general interest. The continuous dissolver proved to be an exceptionally effective device. The control of the dissolver solution by variation of catalyst injection with a constant acid feed stream was quite successful. The plant data obtained showed that the operating characteristics of the 7½-in.-diameter plant continuous dissolver were similar to the pilot-plant 2-in. and 5-in. dissolvers.

Product quality with long-cooled alloy was exceptionally good. Beta ratios\* of 1 or 2 were obtained consistently. However, when Materials Testing Reactor (MTR) feeds were processed, product beta ratios up to 60 were experienced, and product recycle was required. The poor beta decontamination of the MTR feeds is attributed to the aging characteristics of ruthenium in this feed, which resulted in an unfavorable distribution of extractable and nonextractable ruthenium.

Three-cycle gross beta and gamma decontamination factors of about  $10^6$  have been indicated in plant samples. The result for gross decontamination is essentially equivalent to the result experienced with three hexone cycles and leads to the conclusion that the decontamination efficiency for the two-solvent system on this flow sheet has not been proved to be superior to the three-hexone-cycle performance.

In-line monitoring of radioactive process streams by a detector cell placed in the stream is a useful and widely used technique. One of the disadvantages of this system is the tendency for the monitoring cell to adsorb activity, thereby rendering the cell less sensitive to activity fluctuations in the process stream. A report recently released<sup>21</sup> for general circulation deals with the utilization of electrochemical means to control radioactive contamination of a stainless-steel-walled in-line detector cell. In the proposed system the detector cell is electrically insulated from the rest of the process and is used as an electrode

of an electric cell. Experiments were conducted to determine the effectiveness of this technique. Stainless-steel coupons were used to simulate the detector cell. Circuit diagrams of the apparatus used in these tests are shown in the report.

Each test electrode was first electropolished to remove surface scratches and to create an equipotential surface. After electropolishing, the thick surface oxide layer was again restored by dipping in concentrated nitric acid. Observation through a microscope showed the surface to be considerably smoother than it was before electropolishing, although slight etching occurred at the grain boundaries.

The electrodes were 1½- by 1- by ⅛-in. coupons of type 316 stainless steel. In each cell, two cathodes and one anode were supported by type 347 stainless-steel wire and were completely immersed in contaminated dilute nitric acid solution.

A control for each run was obtained by using a coupon immersed in a solution similar to that used in the cell. Gross beta and gamma counts were made on the contaminated coupons using a beta proportional counter. Both sides of the coupon were counted, and the two counts were averaged to obtain the coupon activity. The decontamination factor was calculated as the ratio of the activities of the cell coupon to the control coupon.

The data taken showed that stainless-steel coupons, maintained anodic in contaminated solutions, will absorb only a small fraction of the activity absorbed by unprotected coupons in identical solutions. In addition, it was shown that niobium is the principal contaminant on stainless steel. Anodic protection was found to reduce niobium contamination by a factor of approximately 20 to 30. Current-cycling experiments indicate that decontamination factors of 300 are attainable. Ordinary 60-cycle alternating current does not appear to be effective.

Corrosion rates were excessive (about 60 mils/year) for some of the current conditions investigated, but the lower corrosion rates on most runs indicate that good decontamination can be obtained at tolerable corrosion rates by combining low current densities (0.5 to 5 ma/cm<sup>2</sup>) with cycle times in the 1- to 10-sec range. Anodic protection need not be continuous in order to be effective. One cycled-current run, with anode current flowing only 3 sec/min, gave a decontamination factor of 300.

\*Beta ratio is the ratio of the specific activity of the product to the specific activity of unirradiated uranium aged for nine months.



## Ion-Exchange Processes

### Plutonium Processing by Ion Exchange

At the recent U. S. - U. K. Technical Exchange Meeting,<sup>22</sup> information was presented on the process chemistry of plutonium in both the cation- and anion-exchange systems. In the cation-exchange system, plutonium is sorbed from a 0.25M nitric acid solution; then uranium is eluted with 0.2M sulfuric acid, followed by plutonium elution with 5.7M nitric acid. Hydroxylamine sulfate is present in all solutions to maintain plutonium in the trivalent state. In the anion-exchange system, plutonium as  $\text{Pu}(\text{NO}_3)_6^{2-}$  is sorbed from a 7M nitric acid solution with the metallurgical impurities passing on through the ion-exchange bed. The plutonium is then eluted with 0.26M nitric acid. The ion-exchange processes are carried out both in fixed beds and in continuous column equipment. Fixed-bed units that have been used are 7 in. in diameter by 15 in. deep and 10 in. in diameter by 5 in. deep. The Higgins type continuous ion-exchange contactor<sup>23</sup> has been operated with the anion-exchange system for about two years, and there is now development work in progress on other types of continuous ion-exchange columns as possible replacements for the Higgins unit. The contactors under development include two moving packed-bed contactors, one moving fluidized-bed differential contactor, and one moving fluidized-bed multi-stage contactor.

Information was also reported on the use of amine extraction to replace ion exchange for plutonium-product purification and on the use of a large-scale Higgins continuous ion-exchange contactor for recovery of uranium by anion exchange.

### Recovery and Purification of Actinide Elements

The anion-exchange adsorption behavior of the quadrivalent actinides was compared with spectrophotometric and solubility data by Ryan.<sup>24</sup> The plutonium, neptunium, and uranium species adsorbing on anion exchangers from nitric acid and from calcium nitrate are  $\text{Pu}(\text{NO}_3)_6^{2-}$ ,  $\text{Np}(\text{NO}_3)_6^{2-}$ , and  $\text{U}(\text{NO}_3)_6^{2-}$ . The data indicate that, in the case of thorium,  $\text{Th}(\text{NO}_3)_6^{2-}$  is adsorbed. The presence of distinct maxima in the anion-exchange distributions of the quadrivalent actinides in nitric acid is attributed to the formation of  $\text{HM}(\text{NO}_3)_6^-$  and  $\text{H}_2\text{M}(\text{NO}_3)_6$

at high acidity. The marked similarity between anion exchange of metal complexes and the solubility of quaternary amine salts of these complexes is pointed out.

### Capacity of Dowex 21K for Uranyl Sulfate

Dowex 21K anion-exchange resin has been proposed for one step of a process for the production of uranium tetrafluoride from sulfate ore leach liquors.<sup>25</sup> The rates of sulfate and chloride self-diffusion from different size fractions of Dowex 21K into dilute sodium sulfate and sodium chloride solutions were measured as a function of the solution flow rate through the resin.<sup>11</sup> The solutions were dilute enough (0.0005M) that the resistance to diffusion was largely in the liquid film surrounding the resin. These results should give values for the effective film thicknesses that will be of use in the treatment of uranium ion-exchange data. Preliminary analyses of the data indicate that the ratio of the film-to-particle diffusion for sulfate self-diffusion from 1200- $\mu$  Dowex 21K is approximately 0.020.

### Miscellaneous Ion-Exchange Studies

*Improved Processes for Uranium Recovery.* In an ordinary ion-exchange process for the recovery of metal from a liquid in which it is in solution as a salt, the common practice is to pass the liquid through a bed of exchange material until the material ceases to absorb all the metal in question from the liquid and then to elute the metal from the bed by the passage of an eluant, i.e., a liquid containing an ion taken up by the bed in exchange for the absorbed metal. The metal may be absorbed and eluted as a cation with the use of a cation-exchange material or as an anionic complex with the use of an anion-exchange material.

In a recent British patent, a continuous ion-exchange process is described<sup>26</sup> which claims several important advantages in comparison with the standard batch process. The process involves the following: The solution containing a complex uranium anion or other valuable ion is passed downward through at least two beds of eluted ion-exchange material in separate absorption vessels. When each bed requires elution, it is transferred from an absorption vessel to a tank in which it is washed to remove trapped impurities. Each washed bed is transferred to one of a number of elution vessels

for elution, the eluant passes in series through two or more elution vessels connected in the order in which the bed in them was formed. When each bed in an elution vessel is eluted, it is transferred to an absorption vessel to become the bed through which the solution last flows.

The advantages claimed for this process are as follows: First, there is longer contact time without additional plant. Second, the vessel volumes available for the ion-exchange material are better used, and thus there is improved absorptive capacity. Third, the washing in a separate tank, combined with the movement of the material from one vessel to another, is effective in obtaining excellent cleaning of the material from mechanical fouling. A chemical cleaning process can be inserted very conveniently at regular intervals, or even at every elution.

In another British patent<sup>27</sup> an improved anion-exchange process for uranium recovery is outlined which claims the advantage of mechanical simplicity in operation. Uranium can be recovered from solutions in which it is present (usually in hexavalent form), for example, aqueous solutions of uranyl sulfate in dilute sulfuric acid, by bringing the solution into contact with granules of an anion-exchange material having at the exchange positions basic nitrogen-containing groups, for example,  $\text{NH}(\text{C}_2\text{H}_5)_2^+\text{Cl}^-$ ,  $\text{N}(\text{CH}_3)_3^+\text{Cl}^-$ , and  $\text{N}(\text{CH}_3)_3^+\text{OH}^-$ . The uranium thus adsorbed on the anion-exchange material as the complex uranium sulfate anion can subsequently be eluted from the material as an aqueous concentrate, and uranium can be recovered from the resulting eluate by conventional means.

According to the patent, the anion-exchange material employed is in tubular form, and the uranium solution is caused to flow through the tube to effect transfer of uranium from the solution to the interior anion-exchange surface of the tube. Preferably, the flow of the solution is maintained at a rate such that the flow is turbulent in order to ensure efficient contacting of the solution with the tube's active interior surface.

In one embodiment of the process, the anion-exchange surface of the tube is formed by a vinyl chloride polymer in which at least 1 per cent of the combined chlorine atoms have been replaced with basic nitrogen-containing groups. The term "vinyl chloride polymer" means polyvinyl chloride itself, and products obtained by

polymerizing vinyl chloride with a copolymerizable substance, such as vinyl acetate or vinylidene chloride.

## Volatility and

### Fused-Salt Processes

The volatilities of uranium and plutonium hexafluorides have been proposed as a basis for processing various types of irradiated nuclear reactor fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase-gas phase fluorination processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are also employed in these dry halogenation processes to enhance process control. In this review, results are summarized of engineering experience in handling fused chloride salts, laboratory-scale dissolution of reactor fuels in liquid  $\text{NO}_2$ -HF, dissolution of uranium metal in bromine trifluoride, direct fluorination of reactor fuels, and physical properties of volatile and nonvolatile fluorides.

### Liquid-Phase Processing

*Fused-Salt Processes: Handling of Fused Chloride Salts.* Two fused chloride salt eutectics, binary  $\text{LiCl-KCl}$  and ternary  $\text{NaCl-KCl-MgCl}_2$ , have been used extensively in fuel-processing studies at Brookhaven National Laboratory (BNL) as part of the Liquid Metal Fuel Reactor (LMFR) research and development program. The engineering experience in handling fused salts at BNL since 1950 has been summarized in a recent report.<sup>28</sup>

Since the fused chloride eutectics are subject to rapid reaction with atmospheric moisture, all handling in the liquid state must be done in an inert atmosphere. In addition, since corrosion by the fused salts is greatly enhanced by the presence of oxidizing impurities, all equipment for use in salt preparation or experimental work must be thoroughly cleaned and tested for leaktightness before use. Generally, type 347 stainless steel was used as the container material.

It has been demonstrated that fused chloride salt technology is sufficiently developed that

loops and other experimental equipment can be designed and operated at 500°C with a high degree of confidence. The equipment, which was operated for many hundreds of hours (in some cases thousands of hours), included a large forced-circulation loop and many thermal-convection loops and tanks. Another large salt loop was designed and built as part of a liquid metal-fused salt continuous processing system, but it is not yet in operation.

The specifications used for the fabrication, cleaning, and testing of equipment for salt service are described. All-welded systems, welded by the usual inert-arc procedures, are preferred, but stainless-steel flanged connections with ring type joints have also been found to be satisfactory.

A number of components were tested at the normal operating temperature of 500°C, including pumps, valves, agitators, sightports, samplers, and filters. Bellows-sealed 1/2-in. Y-pattern globe valves gave good service in both static and circulating salt systems. Both stationary and movable resistance type liquid-level probes were used extensively. Pilot-operated pressure transmitters gave good service in conjunction with both orifice and venturi flowmeters.

A procedure is described for preparing pound quantities of pure eutectics. Both eutectics had to be pretreated with a bismuth-magnesium-uranium solution to remove oxidizing impurities before use in corrosion and processing experiments. The results of physical property measurements on the two eutectics, made at BNL and elsewhere, are included in the report.

*Dissolution of Fuel-Element Materials in Nitrogen Dioxide-Hydrogen Fluoride.* Laboratory-scale work has continued at BNL on the nonaqueous nitrogen dioxide-hydrogen fluoride system for processing reactor fuel elements. Various materials of interest in reactor fuel technology have been tested for dissolution in this solvent.<sup>29</sup> Recently,<sup>30,31</sup> data have been obtained which indicate that niobium and beryllium metal will readily dissolve. Uranium, zirconium, and beryllium oxides and uranium carbide also react with the nitrogen dioxide-hydrogen fluoride mixture. Graphite and pyrolytic carbon are disintegrated by the reagent, but they are not consumed. Uranium has been extracted from a uranium carbide-graphite fuel element.

The dissolution reaction is accompanied by the evolution of hydrogen, but not in quantities equivalent to the fluoride which combines with the metal. It is probable that part of the hydrogen is oxidized to water by the nitrogen dioxide. Calorimetric experiments have shown that the heat evolved is greater than the known heat of reaction of hydrogen fluoride with the metal.

The metals are converted upon dissolution to complex fluorides which contain oxides of nitrogen and which have a low solubility in the solvent. Upon heating, these salts decompose to the normal metal fluorides. X-ray analyses have indicated that uranium is present as nitrosylium hexafluorouranate ( $\text{NOUF}_6$ ) which has been prepared from NO and  $\text{UF}_6$ .<sup>31a,31b</sup> The solid hydrolysis products formed when the salt is in contact with moist air have been identified as uranyl fluoride and uranium tetrafluoride.<sup>31c</sup>

Zirconium-base alloy fuels containing uranium can be disintegrated in  $\text{NO}_2$ -HF. The solubility of the uranium complex fluoride in the solvent is not exceeded during the dissolution; however, the zirconium fluoride salt is only slightly soluble, and the bulk of the zirconium appears as an insoluble residue. The recovery of uranium can be achieved by washing the insoluble complex zirconium salt with the solvent and evaporating the solution. The uranium in the residue is converted to uranium hexafluoride by adding an excess of bromine trifluoride and boiling for a few minutes. The results from several tests indicated that only 0.4 per cent of the uranium accompanied the insoluble zirconium salt. The recovery of uranium as uranium hexafluoride has not been as complete as expected, even in tests in which only uranium was present. Further work on the fluorination step will be necessary to illustrate complete uranium removal from systems in which small quantities of zirconium tetrafluoride are present.

Short-term corrosion rates on Monel, Inconel, nickel, and a variety of other metals have been performed under process conditions.<sup>30,31</sup> In the pure reagent the corrosion rates of Monel, Inconel, and nickel are <1 mil/month. However, in the presence of the complex zirconium salt, the corrosion rates for Monel and nickel increased to 5.6 and 3.6 mils/month. Inconel was essentially unaffected by the presence of the zirconium salt. Monel seems to be entirely unsatisfactory in the step involving evaporation of the dissolver solution. However, when cor-

rosion data are obtained over the entire cycle of the process, including evaporation, Monel appears to be satisfactory. Increased corrosion rates have been occasioned by the presence of small amounts of water, by addition of bromine trifluoride to the dissolver solution, and at points of contact between the container and the dissolving material. Construction materials have not been evaluated under exposures to radiation, but it is known that the solvent does not undergo any major change on prolonged exposure ( $6.8 \times 10^8$  rads) to a strong gamma source.

A generalized flow sheet for the nitrofluor volatility process has been published.<sup>31,32</sup> The flow sheet (Fig. IV-5) is applicable for both

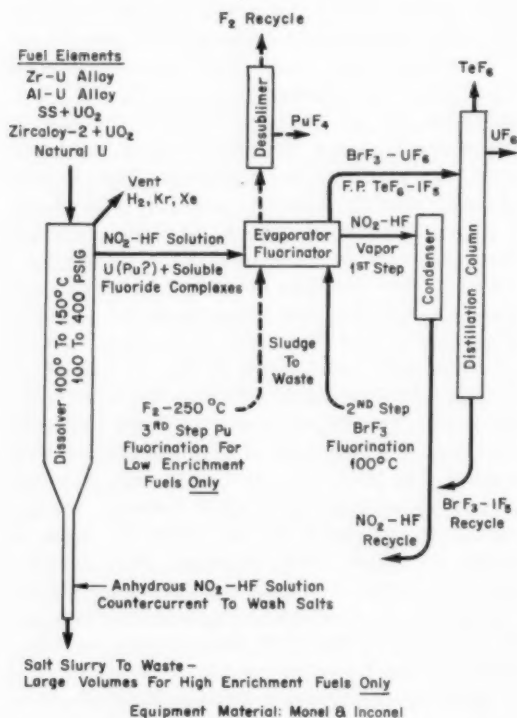


Fig. IV-5 Nitrofluor process flow sheet.<sup>30</sup>

high- and low-enrichment fuels. For low-enrichment fuels a relatively large volume of solvent is required to prevent the precipitation of uranium salt and to maintain a high dissolution rate. The plutonium remains in solution; and, in the case of stainless-steel cladding, no salt washing step is required since the stainless-

steel complexes do not precipitate. After evaporation of the solvent, a two-step fluorination is employed to recover the uranium and plutonium values. The first step is fluorination with bromine trifluoride, which selectively converts the uranium to the volatile uranium hexafluoride. The conversion to plutonium hexafluoride is subsequently carried out by reaction with fluorine. The plutonium may be recovered as the tetrafluoride by thermally decomposing the hexafluoride.

*Dissolution of Uranium Metal in Bromine Trifluoride.* In the bromine trifluoride process for recovery of uranium hexafluoride from uranium metal fuel elements, fluorination is carried out in liquid bromine trifluoride. Studies have continued at BNL<sup>30,31</sup> to determine under what conditions uncontrollable reactions occur. Results on ignition and detonation of uranium metal turnings were reported previously.<sup>33</sup> The dissolution behavior of uranium metal in the form of massive cubes and cylinders has been recently reported.<sup>30</sup> Uranium cylinders  $\frac{3}{4}$  in. in diameter by  $1\frac{1}{2}$  in. long were dissolved in bromine trifluoride, with initial solution temperatures ranging from 118 to 123°C. No submerged ignitions occurred in solutions containing up to 10 mole % uranium hexafluoride.

Uranium in the form of  $\frac{1}{4}$ -in. cubes was also tested for ignition behavior. The cubes were contained in a Monel wire-mesh basket in both random and close-packed (layer) arrangements, which provided internal areas having relatively poor heat-transfer conditions and free access to the liquid reactant. After the cubes were completely submerged in the liquid a few minutes, their behavior ranged from slow dissolution to detonation. Several vapor-phase ignitions were observed when the cubes or remaining pieces were exposed to the vapor. In one test an extremely violent detonation occurred when the basket containing the cubes was two-thirds immersed.

The results suggest that ignition and detonation are more dependent on local temperature conditions which develop during dissolution than upon the initial type of packing or initial solution temperature. Partial exposure to vapor can cause almost immediate ignition or detonation even if the uranium is subsequently immersed in the liquid. There seems to be a difference in the susceptibility of uranium from different sources for producing uncontrollable



reactions. Tests on cubes prepared from Hanford slug material and from cast uranium did not produce detonation, but ignition in the vapor phase did occur. Samples prepared from BNL slugs, however, did produce several detonations during the dissolution tests.

Subsequent tests<sup>31</sup> have shown that ignition and detonation of gamma-extruded natural uranium occur more readily in bromine trifluoride solutions of moderately high uranium hexafluoride concentration (50 to 60 mole %) than in solutions of low concentration (<10 mole %). The effect of hydrogen fluoride concentration on the reaction rate of uranium dissolution is being investigated.

The dissolution behavior of sintered uranium dioxide in bromine trifluoride has been observed.<sup>30</sup> Moderate penetration rates (14 mils/hr) were obtained at 25°C, and extremely high rates (10 in./hr) were obtained at 110°C. Ignition did not occur at the high temperatures, even after the specimens were exposed to the vapor phase. Indications were obtained which showed that uncontrollable reactions can result in this system if fragmentation of the sintered uranium dioxide fuel cylinders occurs.

### Dry Halogenation Processes

Several processes are being developed which involve the separation of zirconium from uranium by volatilization of zirconium tetrachloride. At Oak Ridge National Laboratory (ORNL), the Zircex process<sup>33</sup> is used as a head-end step in which the separated uranium is used as feed to a final decontamination process involving solvent extraction. A similar process under development at BNL<sup>30,31</sup> recovers the uranium by fluoride-volatility techniques.

The Zircex process is based on the use of hydrogen chloride gas at temperatures ranging from 350 to 800°C to convert the zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. This reaction is highly exothermic, and a major problem associated with the process is the removal of heat generated in the reaction. The BNL process utilizes a fluidized bed of inert particles to provide rapid and efficient heat transfer from the reaction zone. Owing to the large heat capacity of the fluidized bed, it is possible to conduct a highly exothermic reaction such as the hydrochlorination of zirconium metal under isothermal conditions. A variety of inert-bed

materials have been evaluated under reaction conditions.<sup>31</sup> Since the uranium, which remains in the fluidized bed after removal of zirconium, will be recovered by fluorination with fluorine, the bed material must be inert to fluorine gas. Various nickel alloys, calcium fluoride, and alumina were evaluated, and only alumina appeared to be satisfactory under all process conditions.<sup>31</sup>

The recovery of uranium from highly enriched uranium-zirconium alloy fuels by reactions with hydrogen chloride or chlorine and hydrogen fluoride gases is being investigated at Argonne National Laboratory (ANL).<sup>34</sup> The process incorporates a two-zone reaction scheme for reacting zirconium with the gases. The fuel element is first reacted with hydrogen chloride or chlorine in the lower part of the fluidized bed to form the volatile zirconium tetrachloride, which in turn is reacted in the upper section of the bed with hydrogen fluoride to form solid zirconium tetrafluoride. The upper zone is separated from the lower zone by a conical baffle that prevents back-mixing of the hydrogen fluoride into the lower reaction zone.<sup>12</sup> The demonstration of this process in a 6-in.-diameter reactor using hydrogen chloride as the primary reacting gas has been reported previously.<sup>12</sup> Since chlorine is less expensive than hydrogen chloride, a series of demonstration runs was made to ascertain its applicability to the process. Appreciably higher rates of attack on uranium-Zircaloy-2 plate assemblies were achieved with chlorine as the primary gas than with hydrogen chloride at temperatures of 350 to 400°C. At chlorine concentrations above 15 vol.% in nitrogen, sufficient heat of reaction was liberated to allow a considerable reduction in the fluid-bed reactor heat input and still maintain a bed temperature of 400°C. Analyses of the particles in the final bed indicate that the uranium and zirconium are uniformly deposited on the particles in the upper zone during the course of the hydrofluorination reaction.<sup>35</sup> The uranium is recovered as uranium hexafluoride by fluid-bed fluorination<sup>12</sup> of the final bed at 500 to 600°C.

Owing to the success of this two-zone concept in converting zirconium-uranium alloy fuels to fluorides, the application of this scheme to the decladding of zirconium-clad and stainless-steel-clad uranium dioxide fuels is being studied. In bench-scale studies<sup>34</sup> the reaction of type 304

stainless-steel tube sections with chlorine has been investigated in a 1½-in.-diameter two-zone fluid-bed reactor. Hydrogen fluoride was admitted to the upper reaction zone above an inverted conical baffle to convert the volatile ferric chloride to the solid fluoride. Initial penetration rates ranged from 6 mils/hr at 570°C to 10.6 mils/hr at 590°C using 100 per cent chlorine as the primary reactant. Since a deposit of nickel chloride forms on the stainless steel during the chlorination reaction, the penetration rate may decrease with time, and these initial rates may not be realized in continued operation. Other primary halogenating agents were tested, but none showed any promise.

An investigation of the corrosive effect of hydrogen fluoride-hydrogen chloride gas mixtures on A-nickel has been initiated. After six days at 500°C, with a 90 vol.% hydrogen chloride mixture, intergranular attack of 0.4 to 1.0 mil was noted. Under these same conditions the penetration rate was 0.023 mil/day as calculated from the weight change of the test coupons. Owing to the short durations of these experiments, the values should be considered preliminary in nature.

#### Direct Fluorination Processes

A direct fluorination volatility process is being developed at ANL to recover uranium and plutonium from spent uranium oxide, Zircaloy-clad, fuel elements. A proposed processing procedure utilizes the reaction of zirconium with a mixture of hydrogen fluoride and hydrogen chloride for decladding. (This is discussed in the previous section on dry halogenation processes.) Plutonium and uranium hexafluorides, which result from the reaction of the oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination of the plutonium and uranium compounds and chemical reactivities of the hexafluorides. Equipment has been constructed and is in operation to study the process steps with multigram amounts (10 to 100 g) of plutonium.

*Fluorination of Uranium Dioxide Pellets.* The dense pelleted fuel material has been shown to be capable of fluorination at a practical rate. Although dense pellets of the kind employed in several nuclear reactors are too large to be fluidized directly, inert fluidizable material to cover and fill the void spaces of the packed bed

of pellets has been used to achieve some of the advantages of fluidization for gas-solid reactions, particularly with respect to heat transfer and temperature control.

The fluorination of uranium dioxide seems to proceed in two steps: (1) uranyl fluoride is produced as fines, and (2) the uranyl fluoride reacts with fluorine to form uranium hexafluoride. During the course of several demonstration runs,<sup>34</sup> it was noticed that the rate of uranium hexafluoride production was low at the start of the run. When the fines (uranyl fluoride) concentration increased, then uranium hexafluoride was produced at a rate corresponding to the fluorination of uranyl fluoride. Deep pellet beds and low fluorination temperatures tended to produce a large amount of fines. The production of a large amount of fines at low temperatures indicates the strong dependence on temperature of the reaction of uranyl fluoride to form uranium hexafluoride.

Fluorination of a 6-in. bed of ¼-in. inert-fired pellets was carried to completion in 6.5 hr with satisfactory reaction control at 500°C and 20 per cent inlet fluorine concentration. Other runs made with pellets that had been hydrogen fired indicated a significantly lower reactivity than the inert-fired type. Successful fluorinations were made with hydrogen-fired pellets at temperatures up to 500°C and inlet fluorine concentrations up to 40 mole %.

*Study of the Chemistry and Separation of Plutonium Hexafluoride and Uranium Hexafluoride.* An investigation<sup>35</sup> of the kinetics and mechanism of the decomposition of plutonium hexafluoride vapor suggests that the reaction is both homogeneous and heterogeneous at 161°C.

Investigation of the stoichiometry of the reaction of plutonium hexafluoride with sulfur tetrafluoride has been completed.<sup>35</sup> The resultant products are sulfur hexafluoride and plutonium tetrafluoride. The reaction of sulfur tetrafluoride with plutonium dioxide at 600°C to produce plutonium tetrafluoride was found to be slow. The investigation of the stoichiometry of the reactions of sulfur tetrafluoride with uranium trioxide, uranium dioxide, uranyl fluoride, and U<sub>3</sub>O<sub>8</sub> has been completed. Uranium hexafluoride is produced equivalent in amount to uranium in the plus-six valence state in these compounds.

Radiation decomposition of plutonium hexafluoride in the presence of uranium hexafluoride

ride, 2.6 per cent per day, was found to be very similar to the value obtained for plutonium hexafluoride alone. Uranium hexafluoride decomposed to the extent of 0.3 per cent per day in the mixture in the gaseous state.

Additional studies of metal fluorinations have been concerned with the mechanisms of the nickel-fluorine and nickel-oxygen reactions. The fluorine reaction appears to occur at the nickel fluoride-nickel interface. In the nickel-oxygen reaction, nickel ions migrate through the nickel oxide, and the reaction with oxygen occurs at the nickel oxide-nickel interface.

### Physical Properties of Volatile

#### and Nonvolatile Fluorides

In an effort to obtain evidence that uranium hexafluoride forms compounds with metal fluorides, a series of experiments was made at ANL where the  $F^{18}$  exchange between uranium hexafluoride and metal fluorides was measured.<sup>36</sup> With radioactive  $F^{18}$  in either sodium fluoride or uranium hexafluoride, exchange experiments indicated complete exchange for a compound of the composition  $2NaF \cdot UF_6$ . In experiments where the amount of uranium hexafluoride present was equivalent to give a compound  $3NaF \cdot UF_6$ , previously reported, the extent of fluorine exchange again indicated that the compound  $2NaF \cdot UF_6$  was formed. Essentially no exchange occurred, and no compound was formed between uranium hexafluoride and lithium fluoride, potassium fluoride, zirconium tetrafluoride, and silver fluoride. A significant amount of exchange was observed between uranium

hexafluoride and calcium fluoride, but no compound was identified.

Chlorine trifluoride is the most reactive of the known halogen fluorides and has been considered as a fluorinating agent in fuel processing. A comprehensive review of the physical and chemical properties of chlorine trifluoride has been published recently.<sup>37</sup> Considerable reference is made to the properties of binary and ternary systems which include chlorine trifluoride.

A comprehensive review of the methods of preparation and the physical properties of the transition metal fluorides has been published recently.<sup>38</sup> Also included is a complete coverage of the properties of the oxyfluorides and complex oxyfluorides. This article is an excellent source of information on many fluorides that have been identified and characterized only recently.

A detailed study<sup>39</sup> has been made on the determination of the vapor pressures of the fluorides and oxyfluorides of molybdenum, tungsten, rhenium, and osmium. From these vapor-pressure data, several physical and thermodynamic constants were derived. The boiling point, triple point, and solid-solid transition point for each compound investigated are presented in Table IV-2. Also included are values of the heats of fusion, vaporization, and transition. The boiling points for the pentafluorides of molybdenum, rhenium, and osmium were obtained by extrapolation of vapor-pressure data since these substances disproportionate below the boiling point.

Table IV-2 PHYSICAL CONSTANTS OF TRANSITION-METAL FLUORIDES AND OXYFLUORIDES<sup>39</sup>

Compound	Boiling point, °C	Triple point		Solid-solid transition point		Heat of fusion, cal/mole	Heat of transition, cal/mole	Heat of vaporization, cal/mole
		°C	Mm Hg	°C	Mm Hg			
WF <sub>6</sub>	17.1	2.0	413.2	-8.2	239.9	420	1,400	6,330
ReF <sub>6</sub>	33.8	18.7	436.5	-1.9	153.1	940	2,090	6,860
OsF <sub>6</sub>	47.5	33.4	474.5	-0.4	81.3	1,760	1,970	6,920
IrF <sub>6</sub>	53.6	43.8	518.8	+0.4	61.7	1,190	1,700	7,380
MoF <sub>6</sub>	34.0	17.4	398.1	-8.7	104.7	920	1,960	6,940
MoF <sub>5</sub>	213.6	67.0						12,370
MoOF <sub>4</sub>	186.0	97.2	28.8			1,020		12,090
ReF <sub>5</sub>	221.3	48.0						13,880
ReOF <sub>4</sub>	171.7	107.8	45.2			3,230		14,590
OsF <sub>5</sub>	225.9	70.0						15,680
ReOF <sub>5</sub>	73.0	40.8	237.1	30.0	144.6	1,220	1,339	7,720
ReO <sub>2</sub> F <sub>3</sub>	185.4	90.0						15,700
WOF <sub>4</sub>	185.9	104.7	25.1			2,260		14,230

Nuclear magnetic resonance spectra<sup>39</sup> of tungsten hexafluoride and molybdenum hexafluoride showed a sharp fluorine resonance of the solid at temperatures above the transition point. Below the transition point, the peak broadens out completely, suggesting the cessation of molecular rotation. The solid transition metal hexafluorides have properties similar to the liquid crystal state at temperatures between the transition point and triple point.

The vapor pressure of liquid  $UF_4$  was measured<sup>40</sup> between 4 and 180 mm Hg (1018 to 1302°C) by a combination of the quasi-static method of Rodebush and Dixon [*Phys. Rev.*, **26**: 851 (1925)] and a boiling-point technique. The data are consistent with the extrapolation of the effusion measurements by Ryon and Twichell [Report H-5.388.2(TL-7703), Tennessee Eastman Corporation, Oak Ridge, Tenn., 1947] on solid uranium tetrafluoride. The vapor pressures of the liquid can be represented by the equation:

$$\log P_{(\text{mm Hg})} = -(16,840 \pm 44)/T - 7.549 \log T + 37.086 \pm 0.03$$

Extrapolation of the data to the normal boiling point of 1729°K, with the assumption of a  $\Delta C_p$  of vaporization of  $-15 \text{ cal/deg(mole)}$ , gives a heat of vaporization of  $51.2 \pm 0.2 \text{ kcal/mole}$  at the boiling point. The entropy of vaporization at the normal boiling temperature is 29.7 eu, which is in reasonable agreement with those of other heavy-metal tetrafluorides. The close agreement between the extrapolated effusion measurements (assuming the vapor species to be monomeric) and the measured pressures indicates the absence of associated molecules in the vapor phase.

The heat of formation of zirconium tetrafluoride has been determined by combustions of zirconium in fluorine.<sup>41</sup> The data lead to a preliminary value of  $\Delta H_{f, 298.15}^\circ = -454.5 \text{ kcal/mole}$ .

## Pyrometallurgical Processes

The development of relatively simple methods for the processing of short-cooled fuels is being pursued at several atomic energy sites. The economic advantages of such processes result from minimization of fuel inventories through the ability to process short-cooled fuels and

from the avoidance of several chemical conversions. These advantages are somewhat offset by the necessity of remote fuel fabrication imposed by the relatively low, but sufficient, fission-product removal.

Pyrometallurgical processes are carried out at elevated temperatures, and the metallic fuels are generally retained in the metallic state. In some schemes the metallic state results as an intrinsic part of the process, e.g., electrochemical separations. Similar processes are also being developed for ceramic fuels. Although these processes are not always pyrometallurgical in nature, they are included in this section because of many common features.

## General

Pyrometallurgical processing methods were described in considerable detail during the Advanced Course on Fuel Elements for Water-Cooled Power Reactors given during the summer of 1960 at Kjeller, Norway.<sup>42,43</sup> The first paper<sup>42</sup> contains a systematic description of pyrometallurgical processes and provides an extensive bibliography (44 references). The development of these processes is followed from the pioneering experiments of Spedding in the early forties to the advanced high-temperature developments presently being pursued at several laboratories. Melt refining, liquid-metal processes, and chemical and electrochemical cyclic oxidation-reduction reactions are covered. The engineering and materials problems associated with the development of equipment for these processes are described. In the second paper<sup>43</sup> the EBR-II fuel-processing scheme is used as an example to illustrate a low decontamination process as an integral part of a reactor fuel cycle. The fuel-cycle facility, the specialized equipment, and individual processing steps are described.

Pyrometallurgical processing methods are reviewed in a Japanese paper;<sup>44</sup> melt refining, liquid-metal and fused-salt processes, fractional crystallization, and electrolytic purification are among the subjects covered. Some of these methods are also discussed in a Belgian paper.<sup>45</sup> Progress in the development of pyrometallurgical processing methods at Atomics International has been reported<sup>46</sup> for fiscal year 1960.

Among the 52 papers presented at the Eighth Conference on Hot Laboratories and Equipment



held at San Francisco<sup>47</sup> are several on processing cells and remote handling equipment used in conjunction with pyrometallurgical processing methods.

### Melt Refining

Argonne's EBR-II, now under construction at the National Reactor Testing Station (NRTS) in Idaho, will use pyrometallurgical procedures in an integrated fuel-processing facility. Melt refining, liquid-metal extraction and fused-salt extraction, and fractional crystallization from liquid-metal solutions are processing steps now being studied at Argonne for the recovery and purification of EBR-II fuels. Melt refining will be the first of these procedures to be used. It is a relatively simple process that consists in (1) melting the discharged uranium-fissium alloy fuel in a zirconia crucible that is stabilized with calcium oxide and (2) holding it at a temperature of 1400°C for several hours. This treatment effects the removal of several fission products by volatilization (xenon, krypton, cesium, and iodine) or by oxidative slagging at the crucible walls (rare earths, barium, and strontium). The purified uranium alloy is poured off into a mold. The status of construction and progress in the development of specialized equipment is given in quarterly reports of the ANL Chemical Engineering Division.<sup>34,48</sup>

The EBR-II fuel-cycle facility building<sup>48</sup> was about 80 per cent complete on Mar. 7, 1961. Installation of cell equipment is beginning. Specialized equipment now being designed or built includes the following: two melt-refining furnaces with associated gas-handling systems and control panel board, coffins for fuel and scrap transport, manipulators, cranes, and 5-ft-thick cell windows. A glass radiation-integrating dosimeter is being developed for recording the gamma exposure received by equipment within the argon and air cells of the fuel-cycle facility.

Irradiation tests are continuing on various materials intended for use in the processing cell. The insulation resistance of asbestos-wrapped wire remained >200 megohms after receiving a dose of  $1.69 \times 10^{10}$  rads under anhydrous conditions. Irradiation tests were also carried out to determine the usefulness of various paints as protective coatings for exposed steel surfaces. Some paints containing polished aluminum flake in various binders exhibited little change after receiving integral

doses between  $0.9 \times 10^{10}$  and  $1.6 \times 10^{10}$  rads. Three types of roller-bearing greases were tested after gamma irradiation of 3 to  $5 \times 10^9$  rads. Two of the greases tested gave satisfactory performance for 300 hr. Other radiation-resistant greases have been developed<sup>49</sup> for which satisfactory lubricating properties at elevated temperatures and under exposure to hot carbon dioxide and nuclear radiation are claimed.

In the EBR-II facility the atmosphere is argon, but a nitrogen concentration of up to 5 per cent is possible. Studies have been conducted at ANL<sup>34,48</sup> to determine the type and extent of chemical reactions that irradiated fuel pins might undergo in such an atmosphere prior to melt refining. Figure IV-6 shows the

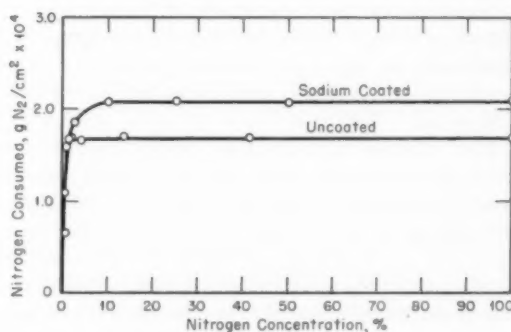


Fig. IV-6 Nitridation of uranium-fissium alloy pins at 308°C for 24 hr.<sup>34,48</sup>

effect of nitrogen concentration on the nitridation rates of uranium-fissium alloy pins, both with and without sodium coatings. The coatings were prepared by subliming metallic sodium onto pins cleaned with a polishing wheel. The nitridation rate was independent of nitrogen concentrations above ~1 per cent for the uncoated pins and ~5 per cent for the coated ones. These rates are such that melt-refining yields may be affected adversely under certain storage conditions.

Melt refining of irradiated uranium is also being studied in Belgium.<sup>50</sup> The specific variables under investigation are the reactions between uranium dioxide and cerium, zirconium, calcium, magnesium, and aluminum contained as impurities in molten uranium; the reaction between thorium dioxide and uranium dioxide; and the influence of the ambient atmosphere composition. In preliminary experiments, ra-

dioautographic techniques showed that homogeneous alloys result from induction melting of unirradiated natural uranium with sufficient cerium or irradiated uranium to give concentrations of 0.5 and 1 per cent, respectively. Rods made from these alloys were first oxidized in air at 200°C to form an oxide dross on the surface and then held for 1 hr in a vacuum furnace at temperatures above the melting point. At tracer fission-product concentrations, the relative concentration of fission products in the metal and in the dross was obtained by gamma spectrometry. It was found that cerium, barium-lanthanum, and iodine were completely removed, and 97 per cent of the zirconium-niobium originally present had been transferred to the dross; the removal of the latter probably occurs through reaction with carbon present in uranium as an impurity. Very little decontamination of uranium from zirconium-niobium was obtained<sup>51</sup> in the melt refining of fissium, in which the zirconium content ranged from 0.15 to 1.86 wt. %.

The release of more than 99 per cent of the inert fission gases contained in metallic uranium irradiated to 300 Mwd/ton was achieved by heating in an air atmosphere at 1200°C for 24 min.<sup>52</sup> Some fission products (barium-La<sup>140</sup>, Cs<sup>137</sup>, and Ru<sup>103</sup>) were collected from a Millipore filter membrane placed in the exhaust duct. The particle size for this material is largely below 0.2  $\mu$  for oxidations at 1200°C, but, for oxidations at temperatures of 1000°C and below, there were only a few submicron particles. When the irradiated uranium (425 Mwd/ton) was heated in helium, only 87 per cent of the rare gases were released.<sup>53</sup> The ratio of uranium to individual fission products in the particles deposited on the filter more closely approximated the ratio in the original specimen for the nonvolatile elements (zirconium, ruthenium, and neptunium) than for the volatile fission products (iodine, tellurium, and cesium).

The "burning" of spent fuel elements, which may occur by accidental overheating, was simulated by induction heating of irradiated uranium specimens<sup>54</sup> up to a temperature of 1800°C. One objective of this study was to gain a better understanding of the physical nature of certain radionuclides and their possible modes of transport to the environs when released from overheated fuels. Iodine-131 was released to the extent of 30 to 40 per cent at oxidation temperatures of 1200 to 1300°C. Electrostatic

precipitators and Millipore filters were tested for fission-product retention.

Studies are in progress at Los Alamos Scientific Laboratory (LASL) to investigate the purification of irradiated plutonium from fission products by liquation and volatilization.<sup>55</sup> The apparatus consists of a tantalum melting crucible with a fine-porosity tantalum filter frit in the bottom made of -100 +200-mesh powder, a tantalum-receiving crucible, and a condenser for volatilized fission products. This equipment was tested first with a stand-in metal and, after installation of the equipment in a sealed glove box, with an unirradiated plutonium-iron alloy. The yield in this experiment was 87.5 per cent of the metal charged as plutonium foil and iron powder. The melt<sup>56</sup> was held for 2 hr at 700°C and for 1 hr at 600°C.

### Processing of Ceramic Fuels

The salt-cycle process, under development at Hanford Atomic Products Operation (HAPO) as part of the plutonium-recycle program, consists of the dissolution of irradiated plutonium oxide-uranium oxide mixture in a sodium chloride-potassium chloride eutectic by the action of chlorine to produce uranyl chloride, followed by electrolytic reduction to uranium dioxide.<sup>52-54</sup>

In recent experiments<sup>52</sup> the dissolution step proceeded smoothly by sparging the molten flux with hydrogen chloride and chlorine. The ratio of uranium to plutonium in the melt remained the same as in the original feed (1050 to 1). Antimony-125 evolved in this step was efficiently removed by the cell filter system. The uranium was separated from plutonium by selective electrodeposition of uranium dioxide. The separation factor for plutonium was ~200, whereas the decontamination factors were 150 for the cerium-praseodymium couple, 1050 for other rare earths, and 90 for strontium.

A three-step flow sheet was proposed for the recycle program:

1. Selective deposition of a fraction of the uranium dioxide, to be discarded as a by-product.

2. Codeposition of a plutonium dioxide-uranium dioxide product at a higher ratio of plutonium to uranium than in the initial feed. This will be recycled as fuel to the reactor. The codeposition of plutonium and uranium dioxides was found to be sensitive to the water and oxygen contents of the sweep gas.<sup>53</sup>

### 3. Replenishment of discarded uranium dioxide with virgin material.

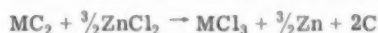
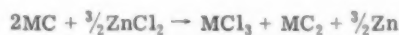
The successful operation of this flow sheet was demonstrated in a second hot-cell experiment<sup>54</sup> with a 220-g batch of irradiated uranium dioxide. In the uranium dioxide by-product separation, decontamination factors were 200 for plutonium, 430 for cerium, and 2000 for other rare earths. The product deposition was preceded by a 2-hr controlled humidity air sparge of the melt. The ratios of plutonium to uranium found in two samples of the mixed oxide product were 6 and 19 per cent, respectively, greater than the ratio which existed in the molten-salt solution prior to the air sparge. By varying the fraction of uranium removed in the by-product deposition, the process becomes sufficiently flexible to accommodate a self-sustaining plutonium-recycle scheme. Over-all decontamination factors were 1.2 for cerium and 6 for other rare earths. The low cerium decontamination is not serious, since this element contributes only a minor poisoning effect; however, procedures will have to be worked out for the other rare earths, which are the most prominent fission-product poisons. Since the only waste stream leaving the process is the uranium dioxide removed in the by-product separation step, the most attractive solution would be to induce the coprecipitation of the rare earths with the uranium dioxide. The salt batch used in this cycle can be reused repeatedly, thus reducing the losses of fertile and fissile materials.

Parallel with the process development work, studies are being made at HAPO which are aimed at elucidating the mechanism of electrodeposition of uranium dioxide from molten sodium chloride-potassium chloride.<sup>52-54</sup> The potential required to initiate deposition of uranium dioxide varies with the nature of the electrode surface, decreasing by about 0.04 volt in the following order: graphite, platinum, and uranium dioxide. Limiting currents that are not responsive to increases in potential can be achieved by concentration polarization. The limiting currents are responsive to gaseous environment over the surface of the melt, their magnitude increasing in the following order: wet helium, dry helium, and dry air. The codeposition of cerium with uranium dioxide can be enhanced by increasing the moisture content of the air under which the electrodeposition

is conducted.<sup>54</sup> The integration of a chemical decladding step into the salt-cycle process is being developed at HAPO.<sup>53</sup> A Zircaloy-clad uranium dioxide fuel pin was declad with molten lead chloride at 550°C. Difficulties were encountered in the recovery of uranium dioxide from this melt by electrolysis.

Thorium dioxide can be dissolved into molten chlorides with hydrogen chloride but not with chlorine. Sparging the resultant solution with oxygen results in quantitative precipitation of the thorium dioxide.<sup>52</sup>

Experiments are in progress at Ames<sup>57</sup> to determine whether uranium and thorium carbide fuels can be processed in a system consisting of molten zinc and a fused potassium chloride-lithium chloride salt bath containing zinc chloride. These reactions are believed to take place in two steps (M = U or Th):



At low zinc chloride concentrations (0.003 to 0.056 mole fraction) and at temperatures between 600 and 790°C, the second reaction did not go to completion.

The possible reaction of uranium monocarbide and thorium monocarbide with liquid zinc was investigated at Ames.<sup>57</sup> There was no reaction in the case of thorium carbide; but, for the uranium monocarbide after equilibration at 500°C, the final zinc microstructure showed two compound phases present, presumably uranium carbide and  $U_2Zn_{17}$ . However, there is a possibility that the uranium-zinc intermetallic may have been formed from unreacted uranium contained in the original carbide. The possibility of reducing uranium carbide in liquid-metal media was also investigated at Argonne.<sup>48</sup> No reactions were observed when uranium monocarbide was contacted at 800°C with the following melts: zinc-0.2 wt.% magnesium, zinc-5 wt.% magnesium, zinc-6 wt.% magnesium-5 wt.% calcium, and zinc-6 wt.% magnesium-4 wt.% calcium with a flux of sodium chloride-magnesium chloride-magnesium fluoride. However, for processing purposes, uranium carbide may be easily converted to uranium oxide, which may be reduced by a zinc-5 wt.% magnesium solution under a molten chloride flux.<sup>48</sup> The oxidation of uranium monocarbide during constant-rate heating

in air was observed to occur over a period of 20 to 30 min between 225 and 600°C, rather than instantaneously, as was expected.<sup>58</sup>

A process is being developed at Atomics International for low-decontamination processing of uranium dioxide fuels in which gases are used to carry out the chemical reactions.<sup>59,60</sup> The technical feasibility of the oxidation-reduction process using oxygen and hydrogen is being investigated for high-burnup uranium dioxide fuels on a 100-g scale. This includes decladding, processing, and refabrication of pellets; loading of capsules; and reirradiation through several complete cycles. In an experiment to observe the behavior of ruthenium, a cumulative decontamination factor of 25 for ruthenium was obtained when irradiated uranium dioxide was oxidized at 100° intervals to 1300°C. Another sample was oxidized at 700°C for 6 hr, during which time the ruthenium decontamination factor reached an essentially constant value of 2. A third sample was carried through five oxygen oxidation-hydrogen reduction cycles at 600°C, in which the cumulative decontamination factor reached 2.4.

The oxidation of uranium dioxide sintered pellets with oxygen at 3 to 800 mm Hg, zero to 450°C, and with a zero to 5 per cent concentration of fission-product oxides (fissia) was studied in an effort to elucidate the kinetics and mechanism of the reactions involved.<sup>61</sup>

A similar low-decontamination procedure for carbide fuels is under development at Atomics International.<sup>59,60</sup> Two approaches are now being considered: (1) the reaction of the carbide with oxygen to yield uranium oxide, which is subsequently reconverted to the carbide by reaction with carbon at elevated temperatures, and (2) the chlorination of the carbide (or oxide produced from the carbide), followed by reconversion to uranium carbide. Differences have been noted in the oxidation behavior of skull uranium carbide and remelted skull uranium carbide. The skull uranium carbide oxidized rapidly, whereas with the remelted material the oxidation rate decreased to a small value after an initial period of rapid oxidation. Work was continued on a study of reaction rate control and heat dissipation during the oxidation of kilogram quantities of uranium carbide. Air oxidation at 300 to 500°C of arc-melted uranium carbide (skull material), using a vibratory sifting apparatus, showed that the vibration provided is insufficient for sifting charges >100

g through 100-mesh screens. The results also indicate that screens at least as fine as 100 mesh are desirable in order to achieve more complete oxidation of the uranium carbide.

In reconstituting the carbide by reacting  $U_3O_8$  with carbon, the product was found to contain carbon in excess of the stoichiometric amount. It is believed that this could be remedied by reducing the  $U_3O_8$  to uranium dioxide before reacting with carbon.<sup>60</sup>

### Liquid-Metal and Salt Processes

Liquid metals and salt systems have been considered as processing media for nuclear fuel materials. These processes usually include one or more of the following steps: dissolution of the fuel material in a suitable liquid metal, selective crystallization, extraction by immiscible metals or molten salts, selective compound formation, volatilization, and selective oxidations and reductions between metal and salt phases using electrolysis or appropriate salts and metals as oxidants and reductants. In liquid-metal processes it is usually desirable to use a liquid metal that can be removed completely by distillation, and thus recover the fissile material. The metals that have been used in these studies are zinc, cadmium, mercury, magnesium, and aluminum (although aluminum does have low volatility).

The chemistry of liquid-metal systems is being investigated at Argonne to provide basic concepts and data for the logical design of pyrometallurgical separation processes.<sup>48</sup> The solubilities of the elements whose separations are being attempted are of prime importance in the design of fuel-processing methods. It is also important to know the dependence of the solubility on temperature and solvent composition. Solubilities have been determined in liquid cadmium for the following elements: terbium, holmium, thulium, ytterbium, and lutetium. The solubilities of these rare-earth metals are shown graphically in Fig. IV-7. Solubilities in cadmium as a function of temperature have also been determined for cobalt, chromium, and titanium. Selected values are given in Table IV-3. Microscopic examination showed that neither cobalt nor chromium forms intermetallic compounds with cadmium. However, the existence of two intermetallic compounds is reported for the titanium-cadmium system.



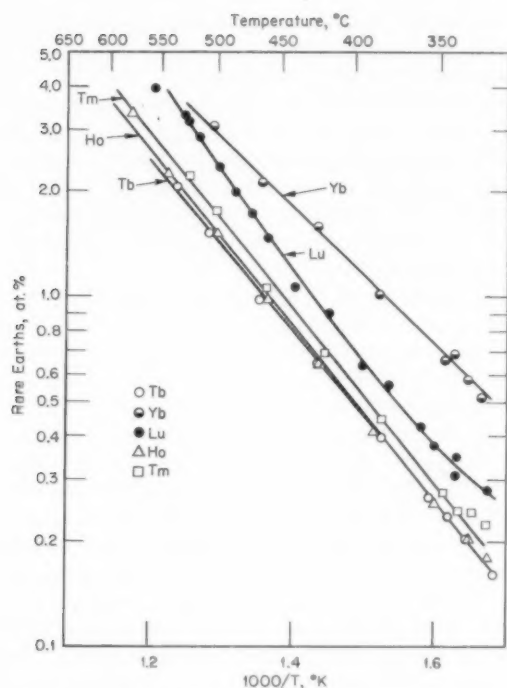


Fig. IV-7 Solubilities of terbium, holmium, thulium, ytterbium, and lutetium in liquid cadmium.<sup>48</sup>

Table IV-3 SOLUBILITIES OF COBALT AND CHROMIUM IN LIQUID CADMIUM<sup>48</sup>

Temp., °C	Cobalt, at. %	Temp., °C	Chromium, at. %
653.4	0.0338	650.6	0.00361
579.4	0.0208	599.9	0.00266
548.4	0.0161	548.4	0.00180
501.5	0.0111	499.6	0.00107
454.5	0.00821	451.0	0.000601
405.4	0.00414		
353.5	0.00386		

Additional values have been obtained<sup>48</sup> for the solubility of uranium in liquid zinc in the temperature range of 822 to 901°C. These data are shown in Fig. IV-8, together with previously reported data for lower temperatures. The solubility of uranium in zinc can be expressed by the following equations:

$$\log (\text{per cent U}) = 6.946 - 6711/T \quad (420 \text{ to } \sim 840^\circ\text{C})$$

$$\log (\text{per cent U}) = 5.87 - 5550/T \quad (\sim 840 \text{ to } 901^\circ\text{C})$$

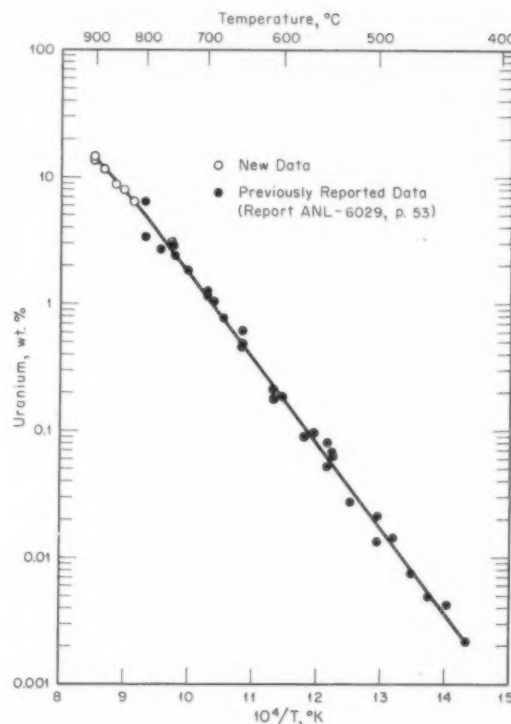


Fig. IV-8 Solubility of uranium in liquid zinc.<sup>48</sup>

The degree of separation which may be achieved by recrystallization from metallic salts is often limited not by the lack of a sufficient difference in solubility but rather by the extent of coprecipitation. Thus, even though the solubility of an impurity is not exceeded when the temperature is lowered, a large fraction of the impurity present may crystallize with the fissionable metal. A systematic study of the influence of several variables, such as atomic radius, metallic valence, and electronegativity, on the coprecipitation phenomenon is being made at Argonne.<sup>48</sup> Coprecipitation coefficients ( $\lambda$ ) have been obtained for a number of elements when carried by  $\text{CeCd}_{11}$  precipitated from liquid cadmium solutions. These coefficients are tabulated in Table IV-4.

Thermodynamic functions for the more important fissionable and fission-product elements in liquid-metal solvents are being determined at Argonne by two methods.<sup>48</sup> Galvanic cells have proved to be especially useful for the measurement of activities in liquid-metal solutions, as well as for the determination of the free energy of formation of the equilibrium



Table IV-4 COPRECIPITATION COEFFICIENTS  
IN LIQUID CADMIUM<sup>48</sup>  
(Carrier in All Cases Is CeCd<sub>10</sub>)

Tracer element	$\lambda$ (coprecipitation coefficient)
Na	0
Li	0
K	0
Y	0
Ba	0
La	$1.49 \pm 0.11$
Th	$1.08 \pm 0.09$
Pr	$0.631 \pm 0.007$
Gd	$0.23 \pm 0.06$
Sm	$0.17 \pm 0.04$
U	$0.13 \pm 0.04$
Sr	$0.10 \pm 0.02$
Eu	$0.099 \pm 0.009$
Sc	$0.05 \pm 0.02$
Zr	$0.04 \pm 0.01$

solid phase in solid-liquid two-phase regions. For systems containing several well-defined intermetallic phases, measurement of the decomposition pressure by the effusion method is proving to be most useful. Effusion studies have been carried out recently for the uranium-cadmium and the cerium-zinc systems.

A liquid-metal process is under development at Argonne for recovery and purification of fissionable material contained in the crucible skulls remaining after melt-refining operation on EBR-II fissium alloys.<sup>48</sup> The flow sheet for the process now under development has been given in a previous Review.<sup>12</sup> This process presently involves removal of a melt-refining skull from a crucible by oxidation to convert it into a powder, selective extraction of noble metals into zinc from a chloride flux-oxide slurry, reduction of uranium and fissium oxides by magnesium in a zinc solution, two uranium precipitations to enable the removal of various fission products in supernatant solutions, and a retorting step to isolate a uranium metal product.

Demonstration runs of the skull reclamation process on a 500-g scale are in progress to pinpoint process problems.<sup>48</sup> Adequate removal (~70 per cent or more) of cerium, molybdenum, and palladium has been shown. The selective extraction step to remove noble metals was not employed in these runs, and hence ruthenium removals were low (~40 per cent). Incorporation of this step should improve the ruthenium removal.

Low zirconium removals were also obtained. The reasons for this are not understood and will require further studies.

The following information was obtained in separate studies of the individual process steps:

—Iodine is the major activity evolved during the oxidation of active melt-refining skulls. A trace of the tellurium activity was also evolved, but no volatilization of ruthenium and molybdenum could be detected.

—Over 80 per cent of the ruthenium, palladium, and molybdenum was extracted into zinc from a fissium oxide flux slurry<sup>48</sup> in 1 hr at 750°C. Separation of phases was readily accomplished by pressure-siphoning off 92 per cent of the liquid zinc phase after solidification of the salt. Analysis showed that the zinc contained only 0.4 per cent of the uranium charged. This procedure is considerably more promising than transfer of the flux-oxide slurry away from the zinc phase because of the difficulty of keeping the oxide in suspension in the flux.

—Further studies on the reduction of uranium oxides by a dilute magnesium-zinc solution in the presence of a chloride flux show that magnesium chloride is an essential ingredient of the flux for rapid and quantitative reductions of U<sub>3</sub>O<sub>8</sub>. The magnesium chloride is usually employed with Group I or Group II element chlorides. Reduction rates decreased with an increase in oxide particle size and a decrease in temperature, although quantitative reductions were achieved at temperatures as low as 650°C.

—Zirconium oxide crucible fragments appearing in skull oxides remained largely unreduced under the conditions employed for uranium oxide reduction and would be removed in the flux phase. However, fission-product zirconium may be more susceptible to reduction than the highly refractory crucible fragments.

In the skull reclamation process, advantage is taken of the low solubility of uranium in high magnesium-zinc systems and the contrasting high solubility of rare earths to effect a uranium-rare earth separation. In the 46 per cent magnesium-zinc eutectic system, the uranium solubility may be reduced from ~0.5 per cent at 800°C to ~0.1 per cent at 400°C. Cerium, at process concentrations, will not be precipitated by cooling to 400°C.

Uranium may be precipitated as agglomerate masses from magnesium-rich zinc systems.

Under various agitation and temperature conditions, the extent of agglomeration has been ~80 per cent. The remaining 20 per cent usually adheres firmly to the tantalum retorting crucibles.

The successful reduction of uranium oxides by zinc-magnesium systems in the presence of a halide flux has prompted application of the procedure to other compounds of interest.<sup>48</sup> Quantitative reductions of uranium tetrafluoride and plutonium dioxide have been achieved. In scouting studies, significant reduction of thorium oxide (65 per cent) was also realized.

Studies are being conducted at Ames on the reduction of fluorides with magnesium-zinc alloys of various compositions.<sup>57,62-64</sup> In experiments on the reduction of a cerium trifluoride, the compositions of the liquid metal ranged from 100 per cent zinc to 100 per cent magnesium. The highest reduction yield (67.0 per cent) was obtained with an alloy of zinc-2.5 per cent magnesium. The reduction yield was zero for pure zinc and only 8.4 per cent for pure magnesium. In each of these experiments, the ingredients were heated to 900°C under an inert-gas atmosphere in a tantalum crucible and agitated with a mechanical stirrer for 1 hr.

Preliminary work has been carried out on the preparation of various compounds by precipitation from liquid-metal solutions.<sup>48</sup> Uranium monocarbide and cerium sesquicarbide (both identified by X-ray diffraction) were precipitated from cadmium-uranium and magnesium-cerium solutions by the addition of finely divided carbon. This general procedure may have important applications in the preparation of fissionable or fertile ceramic reactor materials of high purity and also in the processing of such irradiated materials.

In the current blanket process for EBR-II, the ~1 per cent plutonium-uranium alloy is dissolved in zinc containing magnesium.<sup>48</sup> Additional magnesium is then added after the dissolution to precipitate metallic uranium. The plutonium dissolves in the magnesium-rich phase, thereby accomplishing the desired separation. The plutonium and uranium are recovered by retorting. In two experiments in which this direct dissolution procedure was tried, EBR-II blanket rods dissolved rapidly (within 2 hr). This process is simpler than those previously considered in that the uranium-zinc intermetallic compound is neither precipitated from the solution resulting from

the dissolution of the blanket material nor formed by direct reaction of uranium and zinc at low temperatures. The latter direct reaction procedure was attempted to eliminate the uranium dissolution and intermetallic compound precipitation steps. It was found that massive uranium reacts with zinc very slowly. However, by hydriding and dehydriding the uranium to convert it to a powder of large surface area, a complete reaction was effected within a few hours.

Materials evaluation studies are in progress at ANL to evaluate the compatibility of various materials with liquid-metal systems of the types contemplated for processing reactor fuels.<sup>48</sup> Corrosion studies in the cadmium-zinc-magnesium system indicate virtually no attack of 1020 steel at 750°C by cadmium containing up to 15 per cent zinc. The presence of magnesium appears to be beneficial in reducing any attack. Testing of refractory metals (tantalum, molybdenum, tungsten, and tantalum-tungsten alloys) for containing zinc-based systems is also in progress. Uranium in 5 per cent magnesium solution at 800°C reacts very slowly with grade CS graphite. However, the salt flux penetrates, to some extent, this relatively porous grade of graphite. Since grades of graphite of greater density are readily available, flux penetration is not regarded as a serious problem.

A pilot-plant-scale liquid-metal distillation unit, having a design capacity of 100 kg of cadmium per hour, has been constructed at Argonne and is being tested prior to operation.<sup>48</sup> This unit will permit demonstration of a number of engineering operations encountered in the liquid-metal processes. The preparation of very pure calcium by a method utilizing the distillation and fractional condensation of the raw material has been described.<sup>65</sup>

Atomics International is currently developing new methods for processing thorium fuels.<sup>59,60</sup> One approach is to separate thorium metal by an electrolytic process in which impure thorium is dissolved anodically into a fused-salt bath and deposited in a molten zinc cathode. These experiments have been carried out at 600°C and have led to the production of a zinc-15.2 wt.% thorium alloy. In another application of liquid-metal technology at Atomics International,<sup>59</sup> an alloy of thorium-uranium is dissolved in either magnesium or a magnesium-silver alloy, which is then filtered to separate

the insoluble uranium. One method for recovering thorium from the resulting thorium-magnesium solution is by precipitation of thorium hydride followed by filtration. In an attempt to scale up this process, difficulties were encountered in the hydriding and filtration steps. The uranium recovery in some of these preliminary runs was lower than expected. However, the recovery of thorium was excellent (99 per cent of the thorium charged).<sup>60</sup>

Work has continued at Los Alamos on the electrochemical preparation of special materials in fused-salt baths.<sup>55,56</sup> At the present time, experiments are being conducted on the preparation of plutonium and cerium from metal. The cerium buttons produced by electrolysis were found to consist of  $99.6 \pm 0.1$  per cent cerium. These cerium buttons were cast in alumina crucibles, which accounted for an increase in aluminum impurity values<sup>66</sup> to between 1200 and 2400 ppm. When plutonium was employed, it was found that the final purity of plutonium product was affected by the stability of the casting crucible and the absence of soluble surface impurities. Impurities in the product ranged from 221 to 404 ppm, depending on whether the dendrites produced by electrorefining were melted in a calcia crucible or whether they were cast in an alumina crucible. Another problem has been the removal of free electrolyte from the dendrites formed, without incurring a simultaneous reaction between the solvent and the plutonium product.<sup>54</sup> A preliminary report was issued by Los Alamos<sup>67</sup> covering the production of high-purity plutonium metal by electrolysis on the 100- to 300-g scale. This method was also used to electrorefine a plutonium-10 at.% iron alloy. A product containing <0.02 wt.% iron was obtained.

The potential utility of the partially immiscible liquids lead and zinc in metal separation processes is being investigated at Argonne.<sup>40</sup> The solubilities of cerium and palladium in zinc-lead, as well as the distribution coefficients of these elements between the two phases, are shown in Table IV-5.

Use of various liquid-metal alloys for the decontamination of irradiated uranium by extraction is being studied at Ames.<sup>57,62-64</sup> In equilibration studies of a molten uranium-chromium alloy with silver-magnesium alloys containing 17.8 and 10.6 wt.% magnesium, respectively, it was found that the removal of cesium was extensive (95 per cent). However,

Table IV-5 DISTRIBUTION DATA FOR CERIUM AND PALLADIUM IN THE LEAD-ZINC SYSTEM<sup>68</sup>

Average temp., °C	Solute	Solubility of solute, wt. %		K*
		In zinc layer	In lead layer	
650	Ce	0.24	$1.0 \times 10^{-2}$	24.0
700	Ce	0.21	$1.8 \times 10^{-2}$	11.7
730	Ce	0.21	$3.7 \times 10^{-2}$	5.7
652	Pd	4.3	$2.4 \times 10^{-3}$	1792
703	Pd	4.3	$9.1 \times 10^{-3}$	473
740	Pd	4.1	$2.3 \times 10^{-2}$	178

\*Distribution coefficient  $K = \frac{\text{wt. \% solute in zinc phase}}{\text{wt. \% solute in lead phase}}$

only 20 to 60 per cent of the cesium was found in the extractant, which led to the assumption that the remainder was lost by volatilization. The amount of ruthenium extracted in these experiments was only about 1 to 2 per cent of the amount present in the initial uranium-chromium alloy.<sup>62</sup> A summary of results obtained during the magnesium-silver alloy equilibrations with irradiated uranium-chromium is given in Table IV-6. It will be noted from these results that the effect of increase in magnesium concentration is to increase markedly the distribution coefficient of the rare earths and the alkaline earths fission products. There is also a corresponding decrease in the extraction of plutonium.<sup>63</sup> However, the behavior of plutonium remained unchanged over the magnesium concentration range from 30 to 100 per cent magnesium.<sup>64</sup> Recent results obtained for extractions with either pure magnesium or magnesium-22.6 wt.% silver indicate substantial removal of the following fission products: strontium, barium, and cerium.<sup>57</sup> In extraction studies with a magnesium-cerium alloy, it was found that the addition of cerium to magnesium represses the extraction of plutonium from an irradiated uranium-chromium eutectic alloy.<sup>64</sup>

### Miscellaneous

An apparatus suitable for the study of fused chlorides and fused metals by the dropping bismuth method has been described. This apparatus can be used as an analytical tool and for obtaining physical-chemical information, such as the determination of diffusion coefficients.<sup>68</sup> The interaction of uranium containing molten halide salt mixtures with bismuth was studied.<sup>69</sup>

Table IV-6 SUMMARY OF DATA FROM MAGNESIUM-SILVER ALLOY EQUILIBRATIONS WITH IRRADIATED URANIUM-CHROMIUM EUTECTIC<sup>62</sup>

	Magnesium-silver alloy composition, wt.% Mg			
	51.5	17.8	10.6	0
Plutonium:				
$K_d^*$	1.20	2.25	6.57	21
% removed	26.0	44	75	
Cesium:				
$K_d$	17			2.3
% removed	96.4			
Strontium:				
$K_d$	96	31.7	32.4	8.8
% removed	96.4	95.3	95.3	
Barium:				
$K_d$	94	17.2	18.3	7.9
% removed	97.2	94.9	95.1	
Yttrium:				
$K_d$	1880	176	157	9.1
% removed	99.78	98.7	98.9	
Lanthanum:				
$K_d$	380			9.7
% removed	98.8			
Cerium:				
$K_d$	3440	795	229	18
% removed	99.86	99.7	99.2	
Zirconium:				
$K_d$	0.96	0.51	0.54	1.5
% removed	52.8	43.9	38.1	
Niobium:				
$K_d$	0.12			
% removed	9.2			
Ruthenium:				
$K_d$	0.083	0.028	0.040	0.04
% removed	26			
Tellurium:				
$K_d$	470			3.2
% removed	99.3			

\*  $K_d$  =  $\frac{\text{atom fraction of solute in Mg-Ag phase}}{\text{atom fraction of solute in U-Cr eutectic}}$

A study was made of the over-all rates of the exchange reaction between a bismuth-magnesium-samarium alloy and a sodium chloride-potassium chloride-magnesium chloride eutectic at 500°C by means of the falling liquid-drop technique.<sup>70</sup>

The phase equilibrium relations for the systems limiting the quaternary system LiF-BeF<sub>2</sub>-UF<sub>4</sub>-ThF<sub>4</sub> are described in detail, along with available information on the quaternary system itself.<sup>71</sup>

The solubility of metals in molten salts and also of molten salts in fused metals was reviewed in a recent paper.<sup>72</sup> The miscibility of rubidium metal with its molten halides was found to be large, although it was intermediate between that of potassium and cesium with

their respective halides.<sup>73</sup> The present status and knowledge of fused salts are summarized in an extensive review.<sup>74</sup> A bibliography of 258 references is given.

An attempt was made to correlate surface tensions of liquid metals at the melting point with other properties.<sup>75</sup> A study was published of the ternary system of the chlorides of lithium, potassium, and calcium.<sup>76</sup> Data on the viscosity of several liquid metals and relations between the magnitude of their kinetic viscosities and other physical properties have been published.<sup>77</sup>

Among the topics of interest for liquid-metals technology covered in a recent annual summary report of the Ames Laboratory<sup>78</sup> are the following: a forced-convection loop for circulating liquid lead-bismuth mixtures, vaporization of liquid metals, and liquid-metal extractions.

Published data on embrittlement by liquid metals are collected, reviewed, and evaluated in a recently published book.<sup>79</sup> Among the specialized subjects covered are occurrence of liquid-metal embrittlement, crack propagation, factors influencing embrittlement, delayed failure, theory of metal fracture, and mechanism of liquid-metal embrittlement.

Studies of corrosion and mass transfer of 18-8 stainless steel, mild steel, 5 per cent aluminum-iron, Croloy-5 silicon, Monel, and nickel by a liquid bismuth-lead eutectic alloy were made in a thermal-convection loop.<sup>80</sup>

## Corrosion

Among the various chemical processes that are now being used or are proposed for recovering and decontaminating the uranium and plutonium values of reactor fuels, there are some processes that involve unusually corrosive reagents. AEC contractors have frequently established specific programs for the study of corrosion to aid in the selection of construction materials for such processes. In this section, such programs are reviewed. Where specific programs do not exist, corrosion data may often be found in the section of this Review in which the process is discussed.

## Solvent Extraction

Power-reactor fuels, both those that are in use and most of those that are proposed, may be processed in AEC solvent-extraction plants.



Because of the variety of such fuels, so-called head-end procedures have been developed. These are capable of dissolving the fuels and producing a product that is suited to the existing plants.

The Savannah River Plant is interested in the possible use of their stainless-steel type 309SCb equipment for the processing of zirconium-matrix fuels. In the preceding issue of *Reactor Fuel Processing*, a report on the evaluation of this alloy in various nitric acid-hydrofluoric acid environments was reviewed.<sup>12</sup> The superiority of stainless-steel type 309SCb over type 304L was well demonstrated. The study also indicated that a nitric acid concentration of 1M produced minimum corrosion in solutions of 0.05M to 1M hydrofluoric acid. Additions of zirconium tetrafluoride were found to increase the rate of attack because of the associated increase in fluoride content, in spite of the complexing action that the tetravalent zirconium ion has for fluoride. In a recent series of experiments in which the nitric acid content was held at 1M, the total fluoride content was varied while the free fluoride ion concentration was maintained at a constant 0.4M level.<sup>2</sup> The remaining fluoride was complexed by zirconium ion. The results are shown in Table IV-7. The corrosion rate in the liquid

Table IV-7 CORROSION OF WROUGHT TYPE 309SCb STAINLESS STEEL BY BOILING NITRIC ACID-HYDROFLUORIC ACID SOLUTIONS<sup>2</sup>

Solution composition, M			Liquid corrosion rate, mils/year
HNO <sub>3</sub>	HF	Zr <sup>4+</sup>	
1.0	0.4	0	77
1.0	1.0	0.15	52
1.0	2.0	0.40	57
1.0	3.0	0.65	43

phase showed a modest decrease with increasing zirconium and total fluoride contents. In a plant dissolver the maintenance of a predetermined fluoride concentration level might be achieved by the continuous addition of aqueous hydrofluoric acid during the dissolution of the fuel.

Experiments are being continued at several sites to determine the corrosion inhibiting value of aluminum, zirconium, and thorium in nitric acid-hydrofluoric acid mixtures. Results on the inhibiting effects of aluminum were included in a recent Hanford report.<sup>52</sup> They indicate that,

in nitric acid containing 0.01M hydrofluoric acid, a ratio of aluminum to fluoride of 5 is required in order to reduce the attack on type 304L stainless steel to a level no greater than three times that observed in acid mixtures containing no aluminum and fluoride.<sup>52</sup> Similar experiments were made on two stainless steels in boiling 4M nitric acid-0.6M hydrofluoric acid, both with and without 0.3M aluminum ion. The rate of attack on type 304L stainless steel was reduced from 250 mils/month to 30 mils/month by the addition of the aluminum, whereas for type 309SCb stainless steel the corresponding rates were 30 and 6 mils/month.<sup>52</sup>

The use of the Zirflex and Niflex processes for possible application to zirconium-matrix fuels has been reviewed by BNL in a study supported by the Savannah River Operations Office.<sup>81</sup> The report includes information on the corrosion resistance of stainless-steel type 309SCb to both these processing environments. Preliminary data showed that, with test coupons exposed in a pilot-plant dissolver during dissolution of zirconium fuels, considerably lower corrosion rates were obtained than in standard laboratory corrosion tests of the Huey type in Teflon vessels. Corrosion rates varied from 2 to 11 mils/year in the vapor phase and were 30 to 45 mils/year in the liquid phase. In the section of the report on Niflex dissolution, the effect on corrosion of the method of adding the 49 per cent hydrofluoric acid solution to the dissolver is emphasized. The feed line to the vessel must be designed to prevent splashing of the acid on the walls. It is noted that the inlet nozzle on the pilot-plant dissolver corroded through in a period of 16 hr because the feed line did not extend far enough into the vessel.

SRL has been continuing a series of tests to determine the effect of concentration of solutions containing ammonium fluoride and ammonium nitrate on the corrosion of both wrought and welded type 309SCb stainless steel.<sup>2</sup> All tests were conducted under refluxing conditions. A partial listing of current results is shown in Table IV-8. Results for welded-metal samples were similar and may be found in the original report. Additions of 0.5M zirconium with or without further additions of nitric acid and aluminum nitrate reduce the rate of attack to 13 or <13 mils/year in both phases.

HAPO has been concentrating its efforts relating to Zirflex process environments on the



Table IV-8 CORROSION OF TYPE 309SCb STAINLESS STEEL BY BOILING AMMONIUM FLUORIDE AND AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS<sup>2</sup>

Solution composition, <i>M</i>		Corrosion rate, mils/year	
NH <sub>4</sub> F	NH <sub>4</sub> NO <sub>3</sub>	Liquid	Vapor
3		29	
4		110	11
6		90	
4	0.5	210	14
6	0.5	240	37
4	1.0	290	18
6	1.0	205	25
4*	0.5*	13	5.2
4†	0.5†	2.8	10

\* Sample contained 0.49*M* Zr and 0.004*M* U.

† Sample contained 0.49*M* Zr, 0.004*M* U, 1*M* HNO<sub>3</sub>, and 1*M* Al(NO<sub>3</sub>)<sub>3</sub>.

effect on corrosion of the surface temperature of the metal as influenced by the presence or absence of heat flux in metal samples.<sup>52</sup> The alloy being tested is a new experimental alloy prepared for Hanford by Battelle Memorial Institute (BMI). Designated HAPO-20, it has the following composition (expressed as weight per cent): 50 nickel, 25 chromium, 6 molybdenum, 16 iron, 1 titanium, and 1 copper.<sup>52</sup> In a refluxing environment that simulates a solution expected during zirconium dissolution, the rates obtained under heat-transfer conditions (bulk metal temperature of 135°C and solution at refluxing temperature) were no different from those observed under non-heat-transfer conditions. However, this pattern was altered in a solution of 6*M* ammonium fluoride-0.5*M* ammonium nitrate. With this solution at boiling temperatures, the rate of corrosion under heat-transfer conditions was four to ten times higher than that observed during non-heat transfer. A similar test was conducted on the effect of heat transfer through samples in two Sulfex environment solutions. HAPO-20 alloy was exposed to 4*M* sulfuric acid both with and without stainless-steel dissolution products. The bulk metal temperature was 135°C. Corrosion rates five to ten times higher were observed for heat-transfer conditions as compared to those for non-heat-transfer conditions.<sup>52</sup>

The Darex-Thorex process has been developed as a head-end procedure for stainless-steel-matrix fuels. Titanium is considered to be the leading construction material for the process. ORNL, in the interests of having processes

for both zirconium- and stainless-steel-matrix fuels that are suited to a single installation, is looking into the possibilities of developing a zirconium dissolution process compatible with titanium equipment.<sup>82</sup> The achievement of this objective is a difficult one because of the chemical similarities between titanium and zirconium. The endeavor was aided by the recent discovery that hexavalent chromium in strong acids has a corrosion inhibiting effect on titanium. Earlier experiments indicated that, by using 16*M* nitric acid together with hexavalent chromium and sufficient fluoride to dissolve the Zircaloy-2, titanium corrosion rates could be held to <3 mils/month.<sup>82</sup>

This preliminary information led to a more extended program to determine zirconium dissolution and titanium corrosion rates as a function of the various parameters of the system. The results of the corrosion study are shown in Fig. IV-9. With no chromium in solution, it is evident that a ratio of fluoride to zirconium of <3.5 is required to reduce the titanium corrosion rate to <10 mils/month. With this low ratio, zirconium dissolution proceeds too slowly. Solutions containing 1*M* chromium have reasonably good corrosion characteristics, but these are gained only at the expense of a depressed zirconium dissolution rate. A reasonable compromise is presently thought to be the use of a chromium concentration of ~0.52*M* and operation within ratios of fluorine to zirconium of 3.5 to 5.0. Because of this narrow range of operation, it is thought that a batch process would be difficult to operate, but a continuous process would have a better prospect of satisfactory operation.<sup>82</sup>

The ability to process both stainless-steel- and zirconium-matrix fuels in one plant rather than two has considerable economic advantage. At both ICPP and SRL, electrolytic dissolution of both fuel types is being studied. The selection of construction materials for an electrolytic system involves factors other than those usually considered. At least three specific selections must be made: the anode, the cathode, and the process vessel. Tantalum, niobium, and alloys of these metals with tungsten are, at present, the preferred anode materials. It may be possible, under certain conditions, to use a single material for the cathode and vessel. Current progress at ICPP on the use of Carpenter-20 for cathode and vessel is reported in a recent publication.<sup>83</sup> The data given in this report are

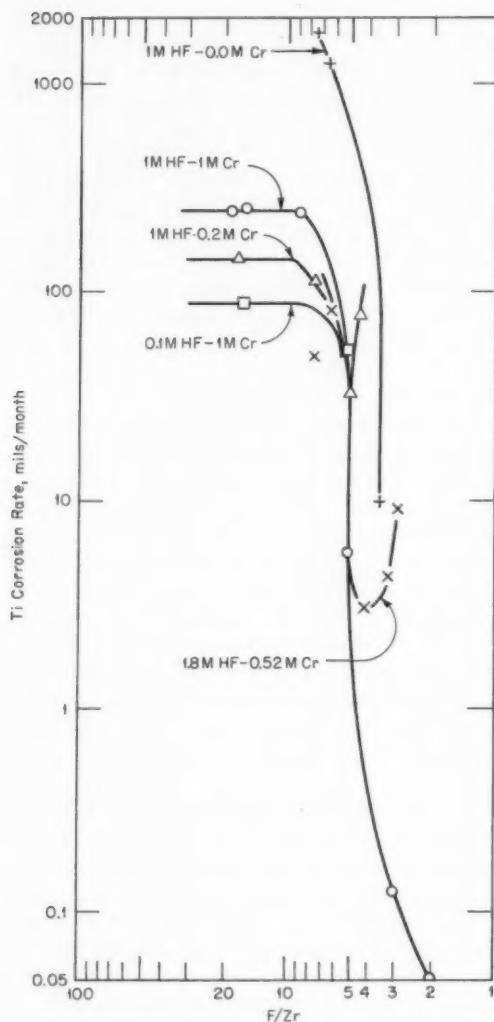


Fig. IV-9 Corrosion rates of 65-A titanium in re-fluxing 16M nitric acid-zirconium solution.<sup>82</sup>

of an exploratory nature, and more extensive studies are indicated. The parameters covered include the concentration of the solution and the current density used. In general, the corrosion rates were below 20 mils/month. The conditions under which corrosion rates above 20 mils/month can be avoided are presented in Table IV-9. Idaho concludes from these results that Carpenter-20 may be used as a cathode if limited life and restrictions on the solution composition can be tolerated. Niobium appears to be acceptable from a corrosion point of view for longer-lived cathodes.<sup>83</sup>

Table IV-9 CONDITIONS UNDER WHICH CORROSION OF CATHODIC CARPENTER-20 IS <20 MILS/MONTH

Current density, amp/cm <sup>2</sup>	Concentrations of the dissolver product solution	
	Nitrate	Hydrogen ion
0.5	>4.5M	>0.5M
1.0	>4.5M	>1.5M
1.5	>6.0M	>3.0M

During the past quarter, three reports, two of them terminal, have been published on the Sulfex process, the Zirflex process, and modifications for the STR fuel-recovery process.<sup>84-86</sup> The corrosion information in these reports has already been presented in preceding issues of this journal. These documents are mentioned here because of their possible use to the reader, since the information on the construction materials is presented in concise form.

#### Fused-Salt and Volatility Processing Methods

A fused-salt process under development at HAPO is directed toward the recovery of uranium from irradiated uranium dioxide fuels. The first step of this process involves the conversion of the  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ , which is then chlorinated with chlorine and hydrogen chloride in an equimolar mixture of sodium and potassium chloride. In a second step, uranium dioxide is deposited at the cathode by electrolysis of the molten-salt solution. Temperatures are 750 to 800°C. Based on preliminary experiments, nickel- or iron-base alloys containing additions of aluminum, molybdenum, and silicon showed the best resistance to the fused salt-chlorine system. Fourteen experimental alloys of these types have been prepared by BMI for testing in the system.<sup>87</sup> These alloys,<sup>88</sup> together with Alnico 3B, Unitemp 600, Hastelloy B, and 68 wt. % nickel-32 wt. % aluminum alloy, were exposed to chlorinated fused salt for 8 hr at 750 to 800°C. The lowest rate of attack observed in specimens exposed below the sparge location was 40 mils/month; the maximum rate was 600 mils/month. It appeared that nickel-aluminum combinations had the lowest corrosive attack. Additions of copper and molybdenum were found to have no effect. Removal of chromium from a Hastelloy C composition resulted in an improved corrosion performance.<sup>88</sup>

In parallel tests conducted at Hanford, various alloys are being exposed to hydrochlorinated

melts and alternate hydrochlorinated and moist-air-sparged melts. Duriron, Durichlor, and Durco D-51 X all corroded at rates in excess of 80 mils/month during a 6-hr exposure<sup>52</sup> to hydrochlorinated melts at 800°C. When Alnico 3B was exposed for 70 hr to melt sparged alternately with hydrogen chloride and water-saturated air,<sup>52</sup> the corrosion rate was 2.5 mils/month. In later tests,<sup>53</sup> three of the Battelle alloys (which were Alnico 3B modifications) and Hastelloy B corroded at rates of <20 mils/month.

Equipment has been assembled at Battelle for an evaluation of the construction materials for the hydrofluorinator of the fused-salt fluoride-volatility process. Conditions simulating the hydrofluorination of oxide type fuels containing uranium dioxide, beryllium oxide, and zirconium dioxide or combinations thereof in either a sodium fluoride-zirconium tetrafluoride or a sodium fluoride-lithium fluoride melt will be studied. The construction material of primary interest is INOR-8 (Hastelloy N), although plans also call for screening tungsten and perhaps some other metals. The assembly has been completed, with the exception of a flowmeter, for the hydrogen fluoride sparge. A shakedown run made without metering the hydrogen fluoride showed that the equipment will perform satisfactorily.<sup>59</sup>

In a proposed process at ANL, the decladding of zirconium- and stainless-steel-matrix fuels is accomplished by submerging the fuel in an inert fluidized bed (such as calcium fluoride or alundum) through which dilute mixtures of halogen gases are passed. At the present time the gases being used are hydrogen chloride or chlorine and hydrogen fluoride in the case of zirconium-matrix fuels and chlorine alone in the case of stainless-steel fuels. In corrosion tests supporting the work on these processes, a number of high-nickel alloys were exposed to chlorine gas above 500°C. A value of 12 mils/month was obtained for Hastelloy C at 600°C, compared to 20 mils/month for nickel and Inconel.

### Corrosion in Waste Calcination

High-temperature calcination appears to offer a method whereby the storage volumes of processing wastes may be reduced. Both laboratory and pilot-plant studies are being made by HAPD and ICPP. In general, the product waste is a

high-density solid having a high concentration of fission products. Where the activity levels are high, it is expected that high temperatures will develop in the storage vessels as a result of beta and gamma heating. A corrosion program was initiated at ICPP through a subcontract with the Fluor Corporation, Ltd., to determine what construction materials would be suitable in the so-called Demonstrational High-Temperature Solids Storage System.<sup>50</sup> Studies were made with three promising materials: Incoloy, Inconel, and type 430 stainless steel. A series of metal coupons, both welded and unwelded, were immersed in beds of calcined alumina, clean silica sand, San Gabriel sand, Idaho wind-blown and pit-run sand, and Johns-Manville Sil-O-Cel insulating powder. Some coupons were protected by 1/2-in. magnesia or 1/4-in. Johns-Manville Serefelt insulation. The beds, which were contained in 4-in.-diameter by 12-in.-long stainless-steel tubes, were heated in an oven to temperatures ranging from 950 to 1700°F for periods of 72 and 150 hr. Control coupons were placed in ceramic dishes exposed to the oven air. The method of evaluation included microscopic surface inspection, bending and microscopic examination of the bend area, and photomicrographs of freshly cut and polished edges. The results of the initial test eliminated type 430 stainless steel as a candidate material. Additional tests were made in which trace amounts of cesium and sodium nitrates in an alumina bed were used. In general, the results were as follows: at temperatures in excess of 1500°F, all alloys suffered significant damage when subjected to an environment of Idaho sand or calcined alumina. Incoloy was found to be more corrosion resistant in sand than Inconel. The reverse was true in calcined alumina. At 1200°F, little attack was observed on either of the high nickel-base alloys. Of the two spiked chemicals in the calcined material, cesium nitrate and sodium nitrate, the latter caused the greater damage. It is concluded from these tests that Inconel's resistance to corrosion was satisfactory up to 1350°F, whereas Incoloy and stainless steels were acceptable to 1200°F. None of the materials tested<sup>50</sup> were found to be satisfactory above 1700°F.

The high-temperature oxidation resistance of Inconel and Inconel X was determined at 1500°F in order to check these alloys for contact with air atmospheres. The average rate of attack

of both welded and unwelded Inconel was ~0.02 mil/month, whereas corresponding values for Inconel X varied between 0.04 and 0.08 mil/month.<sup>91</sup>

### Pyrometallurgical Processing

Pyrometallurgical processing techniques under development at several AEC contractors' sites involve the use of a variety of molten-metal environments. The ability to contain molten uranium in a metallic construction material has long been considered a desirable objective. It has been known for some time that tantalum can be used for experimental purposes where exposure periods are short. Yttrium is undergoing metallurgical development for a similar purpose. In recent information from Ames Laboratory,<sup>62</sup> it appears that niobium may have a potential use in molten uranium-manganese environments. The 94 wt.% uranium-manganese alloy melts at 716°C. Static corrosion tests in a niobium container were run at 825°C for 2800 hr. Attack was found to be <1 mil. Since niobium is more easily fabricated than yttrium and has somewhat better physical properties at elevated temperatures, this observation is of more than routine interest. Construction of a circulating loop to determine erosion and mass transfer characteristics in this environment is planned.

Construction of a loop fabricated from yttrium is also under way.<sup>62</sup> Machined fittings will be used; elbows and tees will be made of extruded bar stock of the highest purity yttrium available. Extrusion gives a finer grain structure and better mechanical properties. However, in spite of this, difficulties are being experienced in welding. Very small cracks appear, usually after the termination of a weld or at the center of a weld crater.

In other work involving yttrium,<sup>62</sup> air oxidation characteristics are being determined as a function of fluorine impurity level. Air oxidation rates at 900°C increase by a factor of 10 when the fluorine content is increased from 100 to 1500 ppm. This sensitivity of the corrosion of yttrium to impurity content appears to be characteristic of this metal in other environments also.

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## Section

## V

## WASTE DISPOSAL

### *Operating Experience*

The solid-waste-disposal operations<sup>1</sup> at ORNL are discussed in a recent status report.<sup>2</sup> Since the beginning of operations, five burial sites have been employed. The first three, now abandoned, were located without prior geological and hydrological explorations. Site evaluation has shown that the preferred place for disposal of radioactive waste in the vicinity of Oak Ridge would be in an area underlain by the Conasauga shale formation.

As a result of yearly increases in the volume of solid waste buried, the 25-acre Burial Ground 4 was filled rapidly, the land requirements increasing from about 1.5 to 5.0 acres per year. Off-site shipments used up about 50 per cent of the area. Linear extrapolation of records of solid waste burial dating back to 1957 led to an estimate that an additional  $2.0 \times 10^6$  cu ft of solid waste will be buried at ORNL through 1964, of which more than 50 per cent is expected to be alpha-contaminated waste. By using depth-to-water maps and restricting the depth of burial to 1 ft above the highest water level, it was determined that approximately  $21 \times 10^6$  cu ft of volume is available for disposal of solid waste.

To improve operations and monitoring, a new trench design was recommended. The bottom of the trench, covered with 6 in. of gravel, is sloped to an asphalt-lined sump at one end in which a 6-in. perforated casing is installed. Two trenches had been completed by February 1961. To test the importance of container integrity to ground-water leaching, waste containers (metal drums containing mostly alpha-contaminated material) were placed upright in one trench and were simply dumped into the other trench. The void space around the waste containers was backfilled with shale and compacted by tamping at the top.

Gravel was then added to provide a base for a 1-in. cap of asphalt, after which the remainder of the opening was backfilled with shale. Monitoring data show that the amount of activity leached from drums dumped into a trench is not greater than that from drums carefully placed in a trench, indicating that the higher cost of stacking does not seem justified. However, long-range effects must yet be evaluated.

It was also recommended that special areas within a burial ground be set aside for specific waste types. In addition to providing better control and operation, this procedure would place the most active and presumably the most hazardous waste in a preferred site within the burial ground. Until recently, trenches containing alpha waste were covered with concrete. Auger holes, 1 to 2 ft in diameter and about 15 ft deep, were used to dispose of extremely high-level waste. In addition, some high-level waste was buried in individual stainless-steel containers. This method of operation was economical and convenient, and, to date, no serious hazards have developed as a result of the operation.

At Chalk River 18,000 gal of a moderately radioactive acid-waste solution was disposed of by conversion to a cement mortar.<sup>3</sup> The drums of cement were enclosed in concrete monoliths buried in sand in the solid-waste-disposal area. The diagram of a model monolith is shown in Fig. V-1.\* The wastes contained beta-gamma activity (2600 curies, including 420 curies of  $\text{Sr}^{90}$ ) and  $\text{Pu}^{239}$  (44.5 g) in addition to salts and acids. Results of soil and water samples taken near the buried wastes showed that the ground water, carrying activity leached from these disposals, had a concentration of

\*Figure V-1 is reprinted here by permission from Atomic Energy of Canada, Ltd.<sup>3</sup>

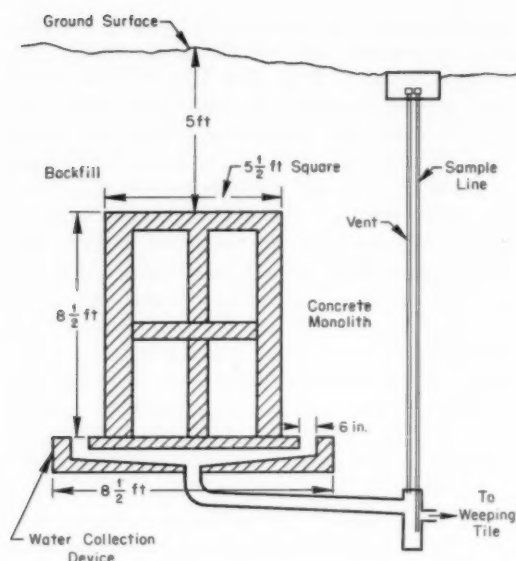


Fig. V-1 Diagram of model concrete monolith.<sup>3</sup>

radioactive material less than the maximum permissible for workers occupationally exposed to radiation for a 40-hr week.

### Low-Level-Activity

### Liquid Waste Handling

The laboratory evaluation of an ion-exchange process<sup>1</sup> for the treatment of large volumes of process-water wastes continues to be studied at ORNL. The treatment consists of a pH adjustment to 12 and a filtration step to remove solids before passage of the water through a bed of cation-exchange resin. Several ion-exchange resins have been tested for their ability to remove radioactivity from these wastes.<sup>4-6</sup> The significant results of these tests are as follows:

1. The sodium forms of Duolite S-30, a pure phenolic resin, and Duolite C-3, a sulfonated phenolic resin, were each tested with an actual water waste containing added  $\text{Sr}^{85}$ ,  $\text{Cs}^{137}$ , and  $\text{Ce}^{141}$  which had been adjusted to a pH of 11.7 and filtered.<sup>4</sup> The Duolite C-3 resin removed about 99 per cent of the activity from about 2000 bed volumes of waste before a breakthrough occurred. Duolite S-30 resin, which showed only half the loading capacity of the C-3 resin, showed better elution characteristics

in that 99.9 per cent of the cesium and strontium was eluted with 3 to 4 bed volumes of 1*M* hydrochloric acid regenerant as compared with 8 to 9 bed volumes of 5*M* hydrochloric acid for C-3 resin.

2. In another run<sup>5</sup> with Duolite C-3 resin using a feed solution similar to the above, cesium appeared in the effluent after passage of 900 bed volumes, and the activity reached 1 per cent of that in the feed after about 1600 bed volumes had been passed through. With mixed fission products the activity of the effluent remained relatively constant at about 2 per cent (principally ruthenium) until breakthrough was reached at about 1890 bed volumes.

3. A feed solution containing added  $\text{Sr}^{85}$  and  $\text{Cs}^{137}$  was tested<sup>6</sup> with Duolite CS-100, a carboxylic-phenolic resin. Thirteen hundred bed volumes were passed through the resin before the 0.1 per cent breakthrough point (decontamination factor = 1000) was reached. Breakthrough of 1 per cent occurred for cesium at about 1700 bed volumes. No strontium activity was observed in the effluent at any time. Upflow elution of this resin with 10 bed volumes of 0.5M nitric acid removed 99.9 per cent of the cesium and strontium. No gassing was observed when the resin was left in stagnant contact with 0.5M nitric acid for 72 hr, but some gassing was noted after five days.

### Reduction to Solids

The work reported in the recent literature on the treatment of high-level liquid radioactive wastes includes the conversion to solid by calcination or by incorporation into glass. The use of minerals for the adsorption of plutonium is also discussed.

### Calcination

ORNL, in its continuing study of the pot calcination<sup>1</sup> of Purex type wastes, investigated the effect of additives,<sup>5,6</sup> (1) on the volatility of ruthenium and sulfates during calcination and (2) on the formation of a meltable solid. Calcination of synthetic Purex waste to 900°C without additives to suppress sulfate volatility gave 34.2, 13.2, and 53.8 per cent of the sulfate in the residue, condensate, and scrubbers, respectively.<sup>5</sup> Heating to 500°C with 1.2 moles of sodium hydroxide (NaOH) and 0.2 mole of magnesium oxide (MgO) per liter gave 37.0.

23.5, 40.9, and 1.4 per cent of the ruthenium in the residue, equipment washings, condensate, and scrubbers, respectively. The fraction of total ruthenium in the condensate was approximately  $\frac{1}{50}$  the fraction of total nitrate in the condensate at any given time until the final high-temperature stage of calcination, when the proportion of volatile ruthenium increased sharply. Some of the ruthenium plated on the metal surfaces in the overhead system, mostly in the deentrainment section rather than in the condenser and evaporator flask.<sup>5</sup> When nitric oxide (NO) was added to the calciner feed stream during semicontinuous evaporation and calcination, 17.6 per cent of the ruthenium was found in the condensate, as compared with 30 to 45 per cent when nitric oxide was introduced into the vapor space of the calciner pot. About 0.43 mole of nitric oxide was consumed per liter of waste solution.

The thermal conductivity of the solids obtained by heating Purex waste to 900°C with added magnesium oxide and sodium hydroxide varied<sup>6</sup> almost linearly with temperature from 0.125 Btu/(hr)(sq ft)(°F/ft) at 300°F to 0.360 at 1350°F.

The addition of phosphorous acid ( $H_3PO_3$ ) to Purex waste before batch calcination decreased the ruthenium volatilized from 21 per cent to 1.9, 0.04, and 0.03 per cent when the solution was 0.61M, 1.52M, and 3.05M, respectively, in phosphorous acid. In a mixture heated to 900°C, boron oxide ( $B_2O_3$ ) and silicon dioxide ( $SiO_2$ ), added to give a glassy melt, did not interfere with the effect of phosphite on the ruthenium. Ruthenium material balances varied between 99.4 and 100.8 per cent.

Sodium sulfate and sodium hydroxide were added to simulated Purex waste, resulting in a solid that (1) melted at ~750°C, (2) increased in weight by 8 per cent (a density of 2.6 g/cm<sup>3</sup>), and (3) decreased in volume by 40 per cent. The large amount of foam in the calciner vessel caused by this feed mixture resulted in plugging of the off-gas line. An average feeding rate of 24 liters/hr was obtained, which is about the same as in runs without melting.<sup>7</sup>

The ICPP NaK-heated, fluidized-bed, 2-ft-square,<sup>1</sup> pilot-plant calciner was operated continuously<sup>8</sup> for 42 days with only minor difficulties in instrumentation and liquid feed systems. The production of two-phase forms of calcined alumina, alpha and amorphous, at apparently the same process conditions was found. On the 11th

day after a 10-day period of apparently steady-state operation, the alumina bulk density increased from 39.3 to 49.0 lb/cu ft, the mass median particle diameter increased from 0.45 to 0.57 mm, and the product rate decreased from 17.5 to 8.9 lb/hr with a corresponding increase in the rate of solids leaving the overhead gas stream. Although this phenomenon is not fully explainable at the present time, the data indicate that the alpha alumina content of the bed exercises a considerable influence over the product properties and calciner performance, a low-alpha content product being definitely more desirable than high-alpha content product. In general, the alumina bulk density and bed attrition increase with increasing alpha content, whereas the residual nitrate content of the alumina decreases. A fundamental study of the mechanism of formation of alpha alumina has been undertaken to determine the conditions required for the production of a low-alpha-content or high-alpha-content bed.

The countercurrent leaching<sup>1</sup> of fission products from calcined alumina is being investigated at ICPP.<sup>8</sup> Calculations of laboratory data indicate that it should be possible to remove 99.9 per cent of the strontium from calcined alumina with 0.5M nitric acid in 2.8 theoretical stages at a solids-to-liquid ratio of 0.05 g/ml. The initial strontium concentration was assumed to be 0.17 mg per gram of calcined alumina on the basis of the analyzed  $Sr^{90}$  concentration in an ICPP first-cycle aluminum nitrate waste storage tank.

The chemical and radiochemical compositions have been determined for the aluminum type wastes that are stored in the four ICPP waste storage tanks now filled and will be used as the radioactive feed to the demonstrational waste calciner.<sup>8</sup> A complete tabulation of these analyses is given in Table V-1.

Studies of gas-cleaning apparatus for the ICPP demonstrational calciner have resulted in the adoption of cyclones and a venturi scrubber followed by an absolute filter as a means of removing alumina particles from the off-gas.<sup>9</sup> By using downstream of the venturi scrubber an electrostatic precipitator<sup>1</sup> for removal of the entrained submicron alumina particles, the scrubber could be operated at lower pressure drops, and the filter would not become rapidly overloaded. It was concluded that a water-film type electrostatic precipitator could be used effectively for removing small concentrations



Table V-1 ANALYSES OF STORED FIRST-CYCLE WASTE AT ICPP<sup>6</sup>

Analysis	Waste tank No.			
	WM-180	WM-182	WM-183	WM-185
<b>Chemical:</b>				
Sp. gr. at 25°C	1.286	1.315	1.263	1.294
H <sup>+</sup>	0.13 <i>N</i> (base)	1.26 <i>N</i> (acid)	0.82 <i>N</i> (acid)	0.59 <i>N</i> (acid)
Al <sup>3+</sup> , molar	1.65	1.72	1.5	1.74
Hg <sup>2+</sup> , g/liter	5.52	4.02	4.11	2.14
NH <sub>4</sub> , molar	1.37	<0.05	<0.05	0.059
Ru, g/liter	0.019	0.027	0.034	0.04
NO <sub>3</sub> <sup>-</sup> , molar	7.10	6.60	5.50	5.40
Fe, g/liter	0.07	0.16	0.29	0.60
Cl <sup>-</sup> , g/liter	<0.005	<0.005	<0.005	<0.001
Te, g/liter	0.0022	0.0061	0.008	0.0077
Mo, g/liter	0.0161	0.067	0.079	0.060
Na, g/liter	0.22	2.4	1.1	0.89
Tc, g/liter	Not reported	0.0074	0.010	0.010
Pu, g/liter	0.0000814	0.0000794	0.000328	0.000453
<b>Radiochemical:</b>				
Gross gamma, † gammas/(min)(ml)	1.73 × 10 <sup>9</sup>	5.35 × 10 <sup>9</sup>	1.15 × 10 <sup>10</sup>	1.25 × 10 <sup>10</sup>
Gross beta, † betas/(min)(ml)	6.48 × 10 <sup>9</sup>	2.18 × 10 <sup>10</sup>	3.77 × 10 <sup>10</sup>	4.94 × 10 <sup>10</sup>
Gross alpha, † alphas/(min)(ml)	3.30 × 10 <sup>5</sup>	6.23 × 10 <sup>5</sup>	1.20 × 10 <sup>6</sup>	1.63 × 10 <sup>6</sup>
Sr <sup>90</sup> , dis/(min)(ml)	1.37 × 10 <sup>9</sup>	2.20 × 10 <sup>9</sup>	3.18 × 10 <sup>9</sup>	2.64 × 10 <sup>9</sup>
Sr <sup>89</sup> , dis/(min)(ml)		1.0 × 10 <sup>9</sup>		9.65 × 10 <sup>8</sup>
Y <sup>91</sup> , dis/(min)(ml)				1.59 × 10 <sup>8</sup>
Zr <sup>95</sup> , dis/(min)(ml)	7.02 × 10 <sup>5</sup>	2.74 × 10 <sup>8</sup>	4.27 × 10 <sup>8</sup>	7.63 × 10 <sup>7</sup>
Nb <sup>95</sup> , dis/(min)(ml)	1.27 × 10 <sup>6</sup>			1.41 × 10 <sup>8</sup>
Ru <sup>106</sup> , dis/(min)(ml)	6.81 × 10 <sup>7</sup>	6.37 × 10 <sup>8</sup>	9.48 × 10 <sup>8</sup>	1.62 × 10 <sup>9</sup>
Cs <sup>137</sup> , dis/(min)(ml)	1.72 × 10 <sup>9</sup>	3.43 × 10 <sup>9</sup>	4.14 × 10 <sup>9</sup>	5.83 × 10 <sup>9</sup>
Ce <sup>144</sup> , dis/(min)(ml)	6.43 × 10 <sup>9</sup>	6.83 × 10 <sup>9</sup>	1.69 × 10 <sup>10</sup>	2.91 × 10 <sup>10</sup>
Co <sup>60</sup> , dis/(min)(ml)	3.13 × 10 <sup>5</sup>	7.86 × 10 <sup>5</sup>	1.34 × 10 <sup>6</sup>	1.02 × 10 <sup>6</sup>

\*Approximately 95 per cent Pu<sup>239-240</sup>.

†An average counting efficiency was used to calculate gross activities from measured values. Since counting efficiency is energy dependent, the gross values given serve only to show relative activities of the various tanks.

of alumina particles <1.2  $\mu$  in diameter. Efficiencies of 98.7 to 99.5 per cent were obtained in a water-film single-stage precipitator when the incoming particle loading ranged from 0.9 to  $14 \times 10^{-3}$  grain of alumina solids per cubic foot of gas. At 20 to 25 kv, the exit loading was  $0.5$  to  $10 \times 10^{-5}$  grain per cubic foot, which is within allowable solids concentrations ( $2$  to  $12 \times 10^{-5}$  grain/cu ft) in the off-gas discharged to the stack. These limits are based on allowable concentrations of Sr<sup>90</sup> at the perimeter fence as given by *National Bureau of Standards (U. S.) Handbook No. 69*.

Laboratory experimentation at the ICPP<sup>6</sup> has indicated the feasibility of calcining, in stainless-steel equipment, zirconium-fuel-waste processing solutions<sup>10</sup> containing fluoride ion. A synthetic waste solution ( $0.4M$  zirconium,  $0.67M$  aluminum,  $2.6M$  fluoride ion, and  $1.8M$  nitrate ion) was treated with calcium oxide to yield a slurry that was calcined at  $500^\circ\text{C}$  without detectable volatilization of fluoride. The

resulting calcined solid was found to be highly water insoluble. On the basis of these preliminary results, a detailed study is to be undertaken.

New waste-treatment methods<sup>1,8,10</sup> continue to be explored at ICPP. Mercury cathode electrolysis<sup>1</sup> is being investigated for the separation of fission products from iron, nickel, and chromium in acidic stainless-steel wastes. Zirconium fission product has been determined to be co-removed with the stainless-steel components while strontium and niobium are retained in the aqueous solution.<sup>8</sup> Thus Zr<sup>95</sup> may be a major contaminant in the cathode mercury unless a suitable method is developed to inhibit its removal from the solution. Preliminary data indicate that the stainless-steel alloy components may be separated from the mercury by magnetic separation or air oxidation.

Ion-exchange adsorption with ammonium phosphomolybdate (APM) precipitated on silica gel<sup>10</sup> is being examined for the removal of Cs<sup>137</sup>

from high salt type acidic wastes. Column experiments<sup>8</sup> show that ~2.8 g of APM will remove essentially all the cesium from 1 liter of an ICPP first-cycle aluminum nitrate waste, resulting in an apparent capacity of 21 mg of cesium per gram of APM used, or a true capacity of 92.5 mg of cesium per gram of APM after allowing for APM dissolved and lost from the column.

### Adsorption on Natural Materials

Laboratory experiments with Florida pebble phosphate rock<sup>11,12</sup> at Hanford have shown it to be the most promising of a number of materials studied for removing plutonium from a building sump waste. In one test,<sup>11</sup> using (1) a 21-cm-long column that contained the phosphate-rock mineral having a grain size of 0.25 to 1.0 mm, (2) a flow rate of 1.3 gal/(min)(sq ft), and (3) a residence time of 1.6 min, the first 50 bed volumes of effluent indicated a plutonium decontamination factor exceeding 1000, reducing to a decontamination factor of 20 after passage of 207 bed volumes. At this point the bed had removed 8 mg of plutonium per 100 g of mineral.

In another test,<sup>12</sup> using a flow rate of 1.04 gal/(min)(sq ft) and a residence time of 1.36 min, more than 90 per cent of the plutonium was removed from about 400 column volumes of waste. These columns were eluted with 1.0M sodium carbonate solution, recovering over 95 per cent of the adsorbed plutonium in 5 bed volumes of eluate. This elution converted part of the phosphate mineral to calcite, and it therefore was necessary to regenerate the bed before the second adsorption cycle. After regenerating with 8 bed volumes of 0.1M disodium phosphate, the column was again used to remove plutonium from the sump waste and was found to have slightly better adsorption characteristics than during the first cycle.

### Conversion to Glasses

At Brookhaven National Laboratory, major emphasis is being placed on the formation of phosphate glasses<sup>1</sup> as a means of incorporating fission products in stable media. Of primary interest here is the development of a process in which the entire conversion from the raw aqueous wastes to the final glass product would be carried out in an all-liquid system.<sup>13,14</sup> The results thus far are very promising in this regard and indicate that the phosphate-glass

method offers a number of important advantages and, in particular, lends itself readily to the development of a continuous process in which the liquid media would be transferred by gravity flow from one process (temperature) step to another. Advantages gained through use of an all-liquid system and the separate temperature stages are that problems associated with heat input, removal of decomposition gases, and handling or manipulation of the process materials are minimized, although no mechanical devices or moving parts are required. Two alternative schemes are indicated at the present time, i.e., a semicontinuous process in which the molten glass would be formed directly in individual final storage containers, and a fully continuous process in which the glass would be formed in a central crucible and fed to the storage containers.

The types of waste which appear to be most suitable for incorporation into phosphate glasses are those of relatively low salt content such as Purex and Darex. It has been estimated that volume reductions greater than 160 from the raw waste to the glass product would result in serious decay heat removal problems.<sup>13</sup> Glass cylinders 6 in. in diameter by 5 ft in length with a core temperature of 400°C and an outside wall temperature of 100°C would seem to be suitable.

A Massachusetts Institute of Technology study<sup>15</sup> discusses the conversion of high-level-activity aluminum nitrate type wastes to vitreous fusions. "Porcelain glazes," which are primarily members of the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system, modified in some cases by the addition of varying amounts of alkali-metal or other alkaline-earth oxides as fluxes were selected for investigation. These fusions are among the most refractory of all glazes, are highly insoluble in water and in most alkalis and acids, and are mechanically strong and hard.

Highlights from the conclusions of this study are as follows: Either the liquid waste or the calcined product, as the initial source of aluminum, could be incorporated in fused ceramics formed at temperatures over 1000°C. Volume-reduction factors from the liquid to glass state of up to about 10 to 15 can be obtained. Increasing the flux content increases the solubility of the fused-glass product and decreases the fusion temperatures. Irradiation with gamma rays at doses up to  $10^9$  r have no significant deleterious effect on the solubility of the fused-

glass product. Although cesium is evolved during the firing process, experimental evidence indicates that it is retained in the clay crucible in which the fusion is accomplished (ruthenium volatility was not studied).

At Chalk River, development work on a process for incorporating waste fission products in nepheline syenite glass<sup>16</sup> is essentially complete. In this process, mixed fission products in nitric acid are added to a finely divided mixture of nepheline syenite (a naturally occurring alumina-silicate) and calcium oxide. The resulting gel can be rapidly dried, denitrated, and fused to a leach-resistant stable glass. During the heating, cesium and ruthenium are volatilized. In an investigation concerned only with reducing cesium volatility,<sup>17</sup> this loss was reduced to a fraction of 1 per cent by providing a cover for the mix of fission products and glass-forming material which would trap the cesium and be ultimately incorporated in the glass. This was successfully demonstrated by using a 1- to 2-cm thick layer of powdered nepheline syenite or calcium silicate as a cover material. Glass blocks made by the Chalk River process are now under long-term leaching tests both in the laboratory and in burials below the water table in the field.

## Final Disposal Methods

### Ground Disposal

ORNL is continuing its investigations in the use of solid- or mineral-filled columns in place of seepage pits for the disposal and decontamination of its high pH, intermediate-level-activity liquid wastes.<sup>1</sup> These wastes are presently neutralized with an excess of sodium hydroxide for precipitation of the bulk of the Sr<sup>90</sup>. The supernatant liquid is pumped into seepage pits. A typical analysis of these wastes is given in Table V-2. Vermiculite, variscite (an aluminum hydroxy phosphate), Tennessee rock phosphate, and Florida pebble phosphate, all naturally occurring materials, were studied in the laboratory with synthetic waste solutions to determine the feasibility of their use in columns for the sorption of strontium.<sup>19</sup> All except vermiculite were found to be effective in strontium removal. (However, vermiculite is a satisfactory material for the sorption of cesium.)

Table V-2 CONCENTRATION OF RADIONUCLIDES AND OF CHEMICAL IONS IN ORNL INTERMEDIATE-LEVEL-ACTIVITY WASTES<sup>19</sup>

Radionuclide	Concentration, $\mu\text{c/ml}$	Chemical ions	Concentration, mg/ml
Gross beta	3.5*	Sodium	15
Cs <sup>137</sup>	2.0	Ammonium	0.43
Ru <sup>106</sup>	0.47	Aluminum	0.58
Sr <sup>90</sup>	0.10†	Nitrate	24
Sr <sup>89</sup>	0.038	Sulfate	3.4
Total rare earths	0.40	Chloride	0.20
		Hydroxide	3.5
		Total solids	56

\*Based on a counting efficiency of 12.6 per cent.

†Exclusive of Y<sup>90</sup>.

The strontium-sorption characteristics of vermiculite were improved markedly, increasing from 40 to 92 per cent, when 100 ppm soluble phosphate ion was added to the waste. Similar improvement was also noted when limestone was added along with the vermiculite in a weight ratio of 1 part limestone to 4 parts vermiculite. Decreasing the pH of the solution adversely affected the strontium-removal properties of all the materials, vermiculite being the least effective. In general, for all materials, there was a beneficial, but not marked, effect in strontium sorption with increasing, up to 1000 ppm, calcium ion concentration. Increasing the sodium or strontium concentration did not produce any apparent beneficial effects for strontium sorption. Pilot-scale testing of Florida pebble phosphate was recommended on the basis of these tests and its good structural and hydraulic properties.

The disposal of liquid wastes from Hanford reactors and chemical processing areas is described in a general summary paper<sup>20</sup> contained in the proceedings of the national meeting of the American Society for Testing Materials held in October 1959 in San Francisco. The geography, geology, hydrology of the Hanford site and the waste-technology research concerned with safe ground and river disposal are reviewed.

### Sea Disposal

The AEC awarded two contracts for oceanographic research which would be important in making predictions about ocean current distribution of radioactive isotopes.<sup>21</sup> Actual or

potential sources of ocean-borne radioactivity are fallout from past nuclear detonations, atomic plants located near the seacoasts, low-level wastes disposed of at sea, and the operation of nuclear surface ships and submarines. The study will start next summer (1962) in the mid-North Atlantic Ocean in the vicinity of Bermuda. Eventually, it is hoped that it can be extended to cover all the major oceans.

One of the contracts was awarded to Columbia University's Lamont Geological Observatory, Palisades, N. Y., for a study of the mixing, diffusion, and circulation rates in the oceans. The other was awarded to the Systems Engineering Division of Pneumo Dynamics Corporation, Washington, D. C., for development, fabrication, testing, and delivery of equipment to be used in the ocean current study.

The study will involve placing a commercially available, nontoxic, nonradioactive, fluorescent dye (Rhodamine B) in selected areas of the ocean. It is expected that the dye will remain detectable for a period of approximately one week. Water will be sampled by a ship-towed detecting device containing a fluorometer, which is sensitive enough to record as little as 2 parts of dye per 100 billion parts of water. The project represents the first application of a dye-concentration measurement system for tracer studies of circulation in the deep ocean beyond the continental shelf.

Initial measurements will be made at high ship speed (11 knots) to depths of 200 m (655 ft); later work will be conducted at greater depths, down to 5500 m (18,000 ft) at reduced rates of speed (2 knots).

### *Separation of Specific Isotopes*

ORNL has announced a revised price schedule<sup>22</sup> for Tc<sup>99</sup>, the price dropping to \$100 per gram from \$1600 to \$2800 per gram (depending on quantity). The current output is about 400 g of 99.9 per cent pure Tc<sup>99</sup> per month. This has resulted from an increased availability of technetium from the Paducah operations. Previously only milligram quantities were recovered from fission-product streams. After Savannah River reported that technetium followed the uranium stream in their plant, ORNL made a material balance at Paducah and found most of it in the fluorination residues. ORNL then modified the Paducah system of recovering uranium and

neptunium from the residues to also recover technetium. Technetium, as an aqueous Tc<sup>99</sup> concentrate, then is sent to ORNL for purification. The purification process consists of a multistage solvent extraction with 2,4-dimethyl pyridine followed by crystallization as ammonium pertechnetate from ammonium nitrate solution.

ORNL has also been investigating the recovery, by extraction with tertiary amines, of technetium, neptunium, and uranium from the residues collected in the fluorination of uranium recycled to a gaseous diffusion plant for enrichment.<sup>23-25</sup> Currently these residues are processed for recovery and recycle of the uranium, and technetium and neptunium when present, by leaching with acid aluminum nitrate solution and solvent extraction with TBP. A single-cycle process has been developed which provides coextraction of these three elements with tertiary amine in hydrocarbon solution and separation by consecutive stripping, giving good recoveries and relatively high mutual separation. The chemical flow sheet has been tested in laboratory scale mixer-settler equipment with actual plant feed solution using a commercial tertiary amine (0.3M Alamine 336 in 90 per cent Amsco 125-82, 10 per cent tridecanol). The results, confirming the expected effectiveness of the process, show that the recovery of uranium, neptunium, and technetium were 99.9, 90, and 97 per cent, respectively. The separation of each product from each other was excellent.

ORNL is evaluating the precipitation from an 85 per cent nitrate-ion medium<sup>4,28</sup> of strontium in Purex type wastes as a head-end step treatment prior to employing ion exchange for the recovery of strontium. Data from earlier investigators<sup>27</sup> indicate that barium and strontium can be separated very effectively from such impurities as iron, chromium, sulfate, and rare earths by precipitation in 85 per cent nitric acid. The purified barium and strontium products are then adsorbed on a resin column, and the strontium is recovered separately by nitric acid elution. This proposed scheme would increase the amount of strontium recovered per resin volume used.<sup>4</sup> In two exploratory experiments<sup>26</sup> the Purex waste was diluted with fuming nitric acid until the nitrate-ion content was 85 wt.%. Greater than 95 per cent of the strontium precipitated, but large quantities of the other cations also precipitated, resulting in poor separation. Solubility data indicate that



at least 85 per cent of the strontium precipitated as strontium nitrate.

Hanford is continuing its investigation of recovery and purification of  $\text{Sr}^{90}$  from Purex-plant wastes by solvent-extraction and ion-exchange processes.<sup>1</sup> A head-end treatment step is being proposed for the Purex plant which will furnish a crude-cut concentrate of  $\text{Sr}^{90}$  as a feed-material source.

Laboratory and pilot-plant studies<sup>11,12,28-30</sup> are under way at Hanford for the development of a pulse-column solvent-extraction flow sheet for recovering megacurie quantities of  $\text{Sr}^{90}$  from Purex-plant fission-product crude-cut concentrates. In general, the process proposed, which consists of an extraction-strip cycle and an ion-exchange cycle, relies on the variation in the extraction and stripping behavior of the various Purex waste constituents as a function of pH to enable the required degree of separation and purification of strontium from the other constituents.<sup>28</sup>

A flow sheet<sup>12</sup> that is currently being tested in the pilot plant is as follows:

1. The feed is prepared by complexing the iron, lead, and most of the undesirable fission products with 50 per cent excess EDTA (ethylene diamine tetraacetic acid) and adjusting the pH to 4.2 with sodium acetate and sodium hydroxide.

2. The feed enters the IA column near the mid-point, where it is countercurrently contacted with 0.4M D2EHPA (di-2-ethylhexyl phosphoric acid) plus 0.2M TBP in Shell E-2342 diluent. Under these conditions, all the strontium and calcium and more than 10 per cent of the cerium should be extracted.

3. A scrub stream containing 0.6M citric acid neutralized to a pH of 2.6 to 3.0 is introduced at the top of the IA column. The purpose of this stream is to remove undesirable metal ions and to lower the sodium concentration in the organic product stream.

4. The product overflows to the IB column, where it is countercurrently contacted with 1M citric acid. The flow ratio is adjusted to permit stripping of essentially all the strontium while leaving 75 per cent or more of the calcium and 95 per cent or more of the cerium and other rare earths in the solvent. The product stream leaving the column at a pH of 2.1 to 2.3 with about 5 g of strontium per liter is suitable feed for a cation-exchange column (Dowex 50 resin);

however, for improved cerium decontamination, the pH will probably be adjusted to about 3.

Preliminary results indicate that <3 per cent of the strontium should be lost in the IA column and <5 per cent should be lost in the IB column. The use of partially neutralized citric acid in the scrub solution (IAS) seemed to remove sodium from the solvent effectively.

In the Hanford High-Level Radiochemistry Facility, the ion-exchange equipment was utilized for two full-level production-scale  $\text{Sr}^{90}$  purification runs.<sup>12</sup> Some 13,500 curies of purified  $\text{Sr}^{90}$  were obtained in these two runs. An additional 1500 curies of partially purified material is being held for rework. Mechanical and flow-sheet operation was very satisfactory during the runs. The isotopic purity of the product was  $56.0 \pm 0.2$  per cent  $\text{Sr}^{90}$ , very close to theoretical. The chemical and radiochemical purity was also very satisfactory. The product of the first run analyzed 76.1 wt.% strontium, 11.0 wt.% calcium, 12.1 wt.% copper, and 0.8 wt.% barium. Data on the second run are not complete, but copper was eliminated through a process change, and other impurities are also expected to have been substantially reduced. No radioactivity, other than that due to strontium (and its yttrium daughter), could be detected in either product.

In the first run the purification columns were in the mixed copper-hydrogen cycle. The copper serves as restraining ion to keep the leading edge sharp; and, any cerium and yttrium that may be present collect behind the copper and cause a very high radiation intensity at that point. This intense, localized radiation caused severe gassing and also reduction of some of the cupric ion to metallic copper, an unexpected observation. Both phenomena (gassing and plugging with copper) caused channeling and band tilting. The process was still operable. The metallic copper contributed copper impurity when the  $\text{Sr}^{90}$  product was stripped from the last column with nitric acid. To eliminate these difficulties, calcium was used as restraining ion in the second run and proved very satisfactory. Yttrium (which forms continuously from strontium decay) and any residual cerium passed continuously from the calcium-form column, the bands were very well defined, and gassing was negligible. Copper was still used as restraining ion on the final isolation column; however, the copper was stripped off



with acidic HEDTA (*n*-hydroxyethyl ethylene diamine triacetic acid, which does not displace strontium) as soon as the strontium band had moved onto the column and prior to eluting the strontium with nitric acid. Although this worked satisfactorily, "cold" cerium will probably be used as restraining ion on this column in future runs to eliminate completely the possibility of metallic copper formation. Cerium, like copper, can be removed with acidic HEDTA prior to strontium elution.

For off-site shipment of strontium,<sup>11,12,30</sup> Hanford is studying the calcination of purified strontium nitrate to the oxide form in order to provide a dry free-flowing product that can be more readily packaged.

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## Section VI

## PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

### Uranium

#### Production of Refined Uranium

##### Hexafluoride from Ore Concentrates

In April 1959 the General Chemical Division of Allied Chemical Corporation began delivery of gaseous-diffusion grade uranium hexafluoride produced directly from uranium ore concentrates. The Metropolis, Ill., plant converts ore concentrates to uranium hexafluoride by hydrogen reduction, hydrofluorination, and fluorination in fluidized-bed reactors.<sup>1</sup> Impurities in the uranium hexafluoride are removed by fractional distillation. The plant is designed to process 5000 tons of  $U_3O_8$  per year contained in the ore concentrates. The process is based on development studies performed at ANL which were reported in a previous Review.<sup>2</sup>

The ore concentrates assaying about 70 per cent  $U_3O_8$  are crushed, blended, and fabricated by wet extrusion into pellets of about  $\frac{1}{8}$  in. in diameter and  $\frac{1}{4}$  in. long. After drying at 370 to 540°C, the pellets are crushed to give -40 +200 mesh particles suitable for feed to the fluid-bed reactors. One single-stage reduction reactor operating within a temperature range of 540 to 650°C is sufficient to achieve consistently a minimum of 95 per cent reduction of the concentrate to crude uranium dioxide. The hydrofluorination of the uranium dioxide to uranium tetrafluoride is accomplished in two separate single-stage fluid-bed reactors operating in series with countercurrent solids and gas flow. Crude uranium dioxide is fed directly to the primary hydrofluorinator, where 95 per cent of the conversion to uranium tetrafluoride occurs. The solid product is continuously withdrawn to the secondary reactor, where the conversion is completed by reaction with anhydrous hydrogen fluoride. Both fluid-bed hydrofluorination re-

actors operate within a temperature range of 480 to 590°C.

Particular emphasis during the fluorination step is placed on complete recovery of uranium and utilization of fluorine. This is achieved by employing three fluorination reactors in series. Approximately 80 to 90 per cent of the conversion takes place in the main fluid-bed reaction vessel, with the first and last reactors used primarily for fluorine and residual uranium recovery. An inert bed of calcium fluoride is provided in the fluid-bed reactor to maintain a fluidized bed for heat transfer since nearly all the uranium tetrafluoride feed is consumed during fluorination. The gaseous uranium hexafluoride product is collected in a refrigerated condenser.

Since all three gas-solid reactions are exothermic, considerable emphasis was placed on the design of a simple means for heat transfer from the fluid-bed reactor wall. The present design employs a method of heat removal by forced-air convection. Air at high velocity flows through an annular space between the reactor and furnace walls at a rate regulated by the temperature of the fluidized bed. Both the outer and inner walls of the fluid-bed reactor are provided with fins to increase the heat-transfer surface. The design of the reactors is based on a bed-to-wall heat-transfer coefficient of 30 Btu/(hr)(sq ft)(°F). The fluid-bed reactors are operated at superficial gas velocities in the range of 0.2 to 0.7 ft/sec and at a maximum bed-height-to-diameter ratio of 4.

The fluorides of vanadium and molybdenum are the only impurities present in the crude uranium hexafluoride whose volatilities are such that separation by fractional distillation is required. Molybdenum hexafluoride was identified as the low-boiling key component having a volatility relative to uranium hexafluoride of

1.46. The identity of the high-boiling key component is not established but is apparently an oxyfluoride of molybdenum. The volatility of uranium hexafluoride relative to this material was empirically determined to be 2.16. Due to the limited solubility of vanadium oxyfluoride ( $\text{VOF}_3$ ) in uranium hexafluoride, the concentration of vanadium oxyfluoride limits the degree of low-boiler separation possible without incurring difficulties due to solid deposition in the upper section of the column.

The fractional distillation purification is carried out in two separate Monel distillation columns (Fig. VI-1).<sup>\*</sup> The low-boiler column con-

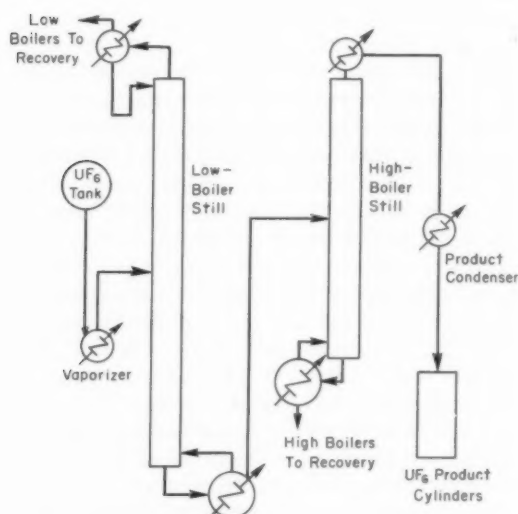


Fig. VI-1 Distillation of uranium hexafluoride.<sup>1</sup>

tains 100 bubble-cap trays and operates at 93°C and 85 psia at the condenser. The small low-boiling fraction is removed from the partial condenser and is processed for scrap uranium recovery. The crude uranium hexafluoride, stripped of low boilers, is distilled in the high-boiler column which contains 45 trays and operates at 115°C and 95 psia at the condenser. The uranium hexafluoride product is liquefied and packaged directly in 10-ton cylinders.

The low- and high-boiling fractions from the distillation columns are processed for recovery of contained uranium by wet chemistry techniques. The reclaimed uranium tetrafluoride is

returned to the process stream in the feed to the fluorination step.

### Uranium Dioxide Production

*Fluid-Bed Reduction of Uranium Trioxide.* Gas-solid reactions, specifically the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rate of these reactions has been shown to be determined by the structure of the solid surface, which in turn is modified by the progress of the reactions. Thermal damage of the solid surface is considerably significant in this type of heterogeneous reaction; and much more so than in the more general fields of combustion and catalysis. The influence of the structure of the solid surface on the choice, design, and operation of a reactor system for the production of uranium dioxide and uranium tetrafluoride is discussed, with considerable emphasis on the fluidization techniques, in a paper by Cooper and Lloyd.<sup>3</sup> The reduction and hydrofluorination reactions demand two prime requirements: (1) uniformity and control of solid-phase reaction conditions, and the ability within the system to program these conditions as conversion proceeds; and (2) efficiency of gas-solid contacting such that economical use of gaseous reactants and high solids conversions can be achieved in the minimum reactor volume. The physical characteristics of uranium trioxide differ widely, depending on how the oxide was prepared; and these differences have a great influence on the subsequent behavior of the solids. Thus the preparation of uranium tetrafluoride is greatly affected by the history of the uranium trioxide.

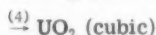
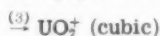
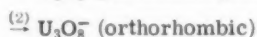
Clayton and Aronson<sup>4</sup> have observed the differences in the physical properties of uranium dioxide produced by variations in the preparation procedure. The crystallite size of uranium dioxide powders seems to depend more on the temperature of preparation than on the method. Low-temperature preparations (350°C) produce the smallest crystallite sizes. The real density of the uranium dioxide product depends to a large extent on the oxygen content of the oxide and on the density of the parent higher oxide. The reduction temperature does not affect the product density, but heating uranium dioxide of low density above the temperature of prepara-

<sup>\*</sup>Figure VI-1 is reprinted here by permission from the American Institute of Chemical Engineers.<sup>1</sup>

tion can cause an increase in density. Measurements indicated that the surface area of the uranium dioxide was dependent on the surface area of the higher oxide and on the reduction temperature. In the reduction of uranium trioxide, the uranium dioxide product was most similar in surface area and particle-size distribution to the parent oxide at low temperatures (480°C). Particle growth occurred at higher temperatures. There seems to be no correlation between the density and surface area of any uranium dioxide preparations.

The successive phase changes that occur during the hydrogen reduction of uranium trioxide have been studied<sup>5</sup> at temperatures of 480 and 750°C. The phase sequence that occurs during the reduction of gamma-uranium trioxide is

Gamma- $\text{UO}_3$  (orthorhombic)



This sequence provides a physical basis for the observed<sup>6</sup> three-step kinetics of gamma-uranium trioxide reduction. Each time a structural change occurs, as in steps 1, 2, and 3, there is also a change in the reaction rate.

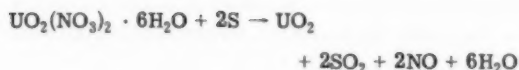
With the present limited understanding of the mechanisms occurring within a fluidized-solids system, it is not possible to apply the apparently simple technique of fluidization in full without added complexity. Thus a cascade of fluidized beds is often required, or the solids mixing pattern is modified by changing the particle-size distribution or by employing a tapered column. A fluid-bed reactor employing an internal tapered mandrel<sup>7</sup> has been tested on a pilot scale for producing uranium dioxide from uranium trioxide by hydrogen reduction at rates up to 100 lb of uranium dioxide per hour per cubic foot of bed. The tapered mandrel permits a close approach to piston flow of the solids in the fluid-bed reactor, provided that the gas velocity does not greatly exceed that required for incipient fluidization. The effect of this flow behavior is that adequate fluidization may be achieved without gross mixing of the fluidized particles. A statistical experimental program involving bed temperature, uranium trioxide feed rate, and hydrogen excess, with

conversion of uranium trioxide to uranium dioxide as the dependent variable, has been performed in a tapered fluid-bed reactor.<sup>8</sup> The uranium trioxide feed was produced by the fluid-bed denitration of uranyl nitrate solutions. The pilot-plant fluid-bed reduction reactor is equipped with an internal mandrel tapered to yield a constant fluidizing velocity from the bottom to the top of the bed. The reactor is 5 in. in diameter and 5.7 ft tall. Centered inside the reactor is a tapered mandrel 53 in. long with a bottom diameter of 2.89 in. tapering to a top diameter of 0.63 in. The experimental results indicated that increased bed temperature, increased hydrogen excess, and decreased production rate all increased the conversion of uranium trioxide to uranium dioxide. The most significant result was that conversion increased as gas flow increased in spite of the additional solids mixing incurred. Uranium dioxide of acceptable quality (uranyl fluoride of 2.3 per cent or less in the resulting uranium tetrafluoride) can be produced at a maximum rate of 90 lb/hr per cubic foot of bed in the single-stage reactor with 20 to 40 per cent excess hydrogen at a reduction temperature of 650°C. With higher hydrogen excess (90 per cent), production of acceptable uranium dioxide at rates slightly greater than 100 lb/hr per cubic foot can be accomplished. The mandrel-in-shell fluid-bed reactor is capable of yielding the conversion of uranium trioxide to uranium dioxide to be expected from a 13-stage reactor at a fluidizing velocity 10 per cent greater than the incipient fluidizing velocity.

*Reduction of Uranyl Nitrate Hexahydrate with Sulfur.* A method for producing uranium dioxide directly from uranyl nitrate hexahydrate by reaction with elemental sulfur has been evaluated in preliminary laboratory tests.<sup>9</sup> Quantitative reduction of 10-g batches of uranyl nitrate hexahydrate was achieved in 5 min at 360°C to yield a black, highly reactive uranium dioxide product. Operation at higher temperatures was not possible owing to the volatility of the sulfur. At temperatures below 270°C, the reaction proceeded very slowly. The reaction product was separated from the unreacted sulfur by extraction of crystalline sulfur with carbon disulfide, followed by vacuum distillation of the remaining sulfur at 300°C. Analyses of the gaseous reaction products indicated that the reaction leading to the production of uranium di-



oxide is



The reaction was observed to be endothermic.

Hydrofluorination studies were carried out at 550°C on products produced at 270, 350, and 360°C. Although some samples contained up to 4 wt. % sulfur, the presence of sulfur did not interfere with the hydrofluorination since it was volatilized prior to the time the sample attained 550°C. In all cases the samples were completely hydrofluorinated (99.6 per cent conversion to uranium tetrafluoride) in 10 min.

*Electrodeposition of Uranium Dioxide.* Separate single crystals of uranium dioxide may be obtained by the electrolysis of uranyl chloride<sup>10</sup> in fused alkali-metal chloride melts. Process variables were studied to obtain conditions that produce uranium dioxide in the form of separate large single crystals. By operating the electrolytic cell at low cathode current density, and at potentials below the apparent decomposition for the reaction  $\text{UO}_2\text{Cl}_2 \rightarrow \text{UO}_2 + \text{Cl}_2$ , uranium dioxide crystals<sup>11</sup> were produced on the cathode at a size of about 3 mm. The electrolytic reduction of uranyl chloride was conducted in an equimolar solution of sodium chloride and potassium chloride at 840°C between a platinum cathode and a carbon anode of large surface area. Carbon cathodes were not used since a reaction takes place on the cathode surface between carbon and uranyl chloride which produces interlocking crystals of uranium dioxide.

It is suggested that two competing reactions occur during electrolysis: (1)  $\text{UO}_2\text{Cl}_2 \rightarrow \text{UO}_2 + \text{Cl}_2$  and (2) a side reaction involving the formation of  $\text{U}_3\text{O}_8$  ions ( $\text{U}_3\text{O}_8^{2+}$ ). The effect of the latter reaction in increasing the oxygen content of the uranium dioxide product can be prevented by the use of carbon anodes, which reduce uranyl chloride by the reaction  $3\text{UO}_2\text{Cl}_2 + 2\text{C} \rightarrow \text{UCl}_4 + 2\text{UO}_2\text{Cl} + 2\text{CO}$ . The uranium tetrachloride produced reacts with  $\text{U}_3\text{O}_8$  ions, forming uranyl chloride which, in turn, is electrolytically reduced at a potential lower than the decomposition potential for the direct reduction of uranyl chloride. Carbon anodes of high surface area were employed to maintain a sufficient concentration of uranium tetrachloride in the melt to preclude the formation of  $\text{U}_3\text{O}_8$  at the cathode.

The optimum concentration of uranyl chloride in the sodium chloride-potassium chloride eutectic was found to be 2.5 wt. %. Operation at an applied potential of 250 mv, and at a cathode current density of 4 ma per square centimeter of cathode area, resulted in a current efficiency of 45 per cent. The electrolytic uranium dioxide product was a crystalline material having a density of 10.8 and a maximum impurity concentration of 300 ppm, of which sodium and potassium contributed 150 ppm.

### Preparation of Uranium Carbides

Uranium monocarbide is 25 per cent more dense than uranium dioxide and has a thermal conductivity at least three times greater than uranium dioxide. These properties, plus the facts that uranium monocarbide (1) has a high melting point, (2) can be cast like a metal, and (3) can withstand neutron irradiations to burn-ups of 1.5 at. % (total), tend to make it the preferred fuel for certain types of nuclear reactors. The common method for preparing uranium monocarbide is the reaction of hydrided uranium metal with hydrocarbons. Diffusion of carbon into massive uranium metal is too slow to permit the carbide to be obtained by reaction of hydrocarbons with massive metal or metal turnings; therefore the metal is pretreated with hydrogen to form finely divided uranium hydride. Since uranium hydride is unstable at the temperatures that are utilized for forming uranium monocarbide, the reaction is actually between the reacting hydrocarbons and uranium metal powder. Decomposition of the hydride apparently produces an activated uranium surface that functions as a catalyst for the decomposition of the hydrocarbons.

Olin Mathieson Chemical Corporation has continued a study on the reaction between uranium metal and hydrocarbons, specifically methane.<sup>12,13</sup> The optimum temperature for the production of pure uranium monocarbide by the reaction of uranium with methane lies between 650 and 700°C. At 600°C, the reaction rate appears to be too slow to be practical. At 700°C, uranium dicarbide is a product of the reaction, whereas below 650°C uranium dicarbide does not form. The presence of excess hydrogen in the reactant gas seems to exert no significant effect on the reaction. Although the presence of combined nitrogen in the uranium monocarbide product does not adversely affect the sintered

density of the carbide, it does tend to replace carbon in the monocarbide structure precipitating uranium dicarbide.<sup>12</sup>

The kinetics of the reaction between uranium and methane have been investigated in a static system.<sup>14</sup> The results seem to indicate that a surface reaction is the rate-controlling mechanism for the uranium-methane reaction and that the hydrogen produced by the reaction remains to some extent adsorbed or associated with uranium carbide.

Propane shows greater reactivity than methane in the preparation of uranium monocarbide. The gas is also attractive because of the high molar concentration of carbon and the low unit cost. Exploratory tests have indicated that products with low oxygen and nitrogen content may be consistently obtained.<sup>12,13</sup> However, the free carbon content of the uranium monocarbide was greater than expected, and there was considerable deposition of carbon on the walls of the reaction vessel. This feature may be corrected by adjusting the reaction conditions.

The reaction of uranium dioxide with graphite to prepare either uranium monocarbide or uranium dicarbide is being studied.<sup>15,16</sup> Studies at ORNL showed that, in the temperature range of 1200 to 1325°C, the reaction yielded primarily uranium dicarbide and followed a parabolic rate equation with an estimated activation energy of 53 kcal/mole.<sup>15</sup> At higher temperatures, up to 2130°C, the parabolic rate equation was found to apply for producing either uranium monocarbide or uranium dicarbide.<sup>16</sup> Contrary to the ORNL data, Craven and McCartney<sup>16</sup> found that, when uranium dioxide and graphite are heated, the first reaction product is uranium monocarbide, and only at temperatures above 2000°C does this compound react with additional carbon to give uranium dicarbide.<sup>16</sup>

Pyrolytic carbon coatings have been applied to uranium dicarbide particles by the fluidized-bed vapor-deposition technique.<sup>17</sup> Carbon was successfully deposited on 150- to 175- $\mu$  uranium dicarbide particles by the thermal decomposition of acetylene at 1350°C. The rate of carbon deposition using a feed gas consisting of 10 to 20 vol. % acetylene in an inert gas was sufficient to produce a 20- $\mu$ -thick coating in 1 hr. The deposits were usually anisotropic.

Although the porosity of the coatings was low, the coatings were occasionally ruptured by heating to temperatures in excess of the signal coating temperature. Coating failure due to

thermal cycling to temperatures above the deposition temperature undoubtedly occurred as a result of the large difference in the coefficients of expansion of uranium dicarbide and pyrolytic carbon. Uranium dicarbide tended to shrink away from the coating when the particles were cooled to room temperature. This thermal-stress problem might be minimized by coating the fuel particles at a temperature higher than the maximum operating temperature expected in the application. A layer of porous carbon adjacent to the uranium dicarbide could be provided to serve as a cushion for expansion.

### Uranium Metal Production

*Reduction from Uranium Hexafluoride.* As reported in a previous Review,<sup>18</sup> uranium hexafluoride has been experimentally reduced directly to uranium metal by a Kroll type process employing either sodium, calcium, or magnesium as reductants. Considerable difficulty was experienced in obtaining a consolidated uranium metal sponge in high yields. In an effort to produce a consolidated uranium regulus, a two-step process has been developed.<sup>19</sup> Uranium hexafluoride is reacted with the reductant at a relatively low temperature—500 to 800°C, depending on the active metal used. The products of this reaction are then treated at a high temperature to complete the reduction and to consolidate the uranium metal. Although the reduction of uranium hexafluoride is complete in the second step at a temperature of 1100°C, a consolidated sponge does not form unless the temperature is raised above the melting point of uranium.

When uranium hexafluoride was introduced into the reactor above the molten-metal reductant, a protective crust formed on the metal surface and prevented complete reaction. To overcome this problem, uranium hexafluoride diluted with helium was injected directly into the molten metal. Several nozzle designs were investigated, and the most successful design consisted of two concentric tubes: helium-diluted uranium hexafluoride was admitted through the inner tube, and pure helium was passed through the annular tube to prevent reaction at the tip of the nozzle.

Considerable attention has been directed toward finding a crucible that will contain the reactants and products without chemical reaction or physical deterioration. Liquid sodium

or magnesium metal tends to penetrate ceramic materials; and, as the temperature is raised above the boiling point of the metal, the liquid contained in the pores of the crucible vaporizes and produces cracking and spalling of the ceramic. Since all common metals alloy readily with uranium, they cannot be used for crucible material during the consolidation of the uranium by melting. The use of magnesium as a reductant is complicated by the fact that magnesium alloys readily with nickel, which is the only metal not corroded by uranium hexafluoride at high temperatures. Several materials (calcium fluoride, boron nitride, and titanium diboride) are being evaluated for crucible construction. Of these, boron nitride appears to be the only suitable crucible material for the reduction of uranium hexafluoride with magnesium.

*Recovery of Uranium Scrap Metal.* Operations at the Weldon Springs feed materials plant generate considerable quantities of scrap uranium metal. Most high-quality uranium scrap is recovered by vacuum casting; however, both ingot lathe turnings and core turnings are not usually recovered in this manner. Ingot lathe turnings are by-products of an operation in which 19-in.-diameter ingots are machined on a vertical lathe. At present, ingot lathe turnings are being produced at the rate of 32 tons per month. Core turnings are produced by machining at much faster rates and with small cuts. This material is more oxidized and nitrified than ingot lathe turnings. Core turnings are presently recovered by burning to  $U_3O_8$  and recycling through the refinery. This route incurs the cost of nitric acid, hydrofluoric acid, and magnesium which amounts to \$0.18 per pound of uranium. A method was investigated for recovering scrap metal by recycle directly to the reduction bomb utilizing the excess heat of reaction in the bomb to melt the scrap.<sup>20</sup> Process conditions were established in 4-kg dingot bombs.

Massive pieces of uranium comprising as much as 7 per cent of the green-salt charge can be remelted in the 4-kg dingot bomb without loss of metal quality. Metal yields decrease, however, because of poor slag-metal separation. The recovery of degreased ingot lathe turnings is generally acceptable at levels up to 13 per cent of the green-salt charge. Core fabrication turnings may be recovered in good yield only when pickled, as well as degreased,

and added to the charge in amounts not exceeding 2 per cent of the green-salt charge. In view of these encouraging laboratory results, the process will be studied on a pilot-plant scale to ascertain whether these findings can be applied to the 3300-lb production dingot bomb.

## Thorium

### Preparation of Thorium Tetrachloride

#### and Reduction to Metal

The U. S. Bureau of Mines Metallurgy Research Center at Albany, Oreg., has initiated the development of a process for the preparation of high-purity thorium metal by the reduction of purified thorium tetrachloride in a manner similar to the Kroll process for titanium and zirconium. Since the objective of the process is primarily the preparation of low-oxygen-content metal, considerable emphasis has been placed on developing methods for the production of pure thorium tetrachloride from thorium oxide.

Although preliminary results<sup>18</sup> indicated that high-quality metal could be produced from purified thorium tetrachloride by reduction with sodium, considerable process refinement of the chlorination step would be required to make the process feasible. The crude thorium tetrachloride product from the horizontal static-bed chlorination of thorium oxide with carbon tetrachloride contained a considerable amount of solid impurities, specifically thorium oxide. High conversion was achieved only with reaction times of over 24 hr. Two distillation purification steps were necessary to produce acceptable material for reduction to metal.

Several alternate methods for producing thorium tetrachloride have been explored to increase the product quality and the scale of operation.<sup>19</sup> A fluidized-bed chlorinator concept, which offers considerably more efficient contact between the reacting gases and solids, was tested. Although it was impossible to maintain a fluidized bed of -325 mesh thorium oxide particles in a 2-in.-diameter column, operation with a 4-in.-diameter unit seemed workable and is currently being evaluated. The use of vertical fixed-bed chlorinators is also being studied. The chlorination of a suspension of thorium oxide particles in a eutectic mixture of sodium chloride-magnesium chloride or lithium chloride-potassium chloride was investigated.

Carbon tetrachloride diluted with argon was bubbled into the fused salt at temperatures ranging from 300 to 600°C. This procedure was ineffective in producing high yields of thorium tetrachloride.

A series of tests were made in an attempt to find a faster, more efficient method of chlorinating thorium oxide. Chlorinating agents evaluated were chlorine and carbon, carbon tetrachloride diluted with helium, carbon tetrachloride with ammonium chloride, chlorine and sulfur dioxide, chlorine and sulfur monochloride, phosgene, and a combination of ammonium chloride and phosgene. Each of these agents was tested at temperatures ranging from 425 to 575°C by passing the gases upward through vertical, fixed beds of thorium oxide. High conversion was achieved with either phosgene or a combination of sulfur monochloride and chlorine at 500 to 550°C. Because of sulfur contamination in the thorium tetrachloride product (0.03 per cent sulfur), purification procedures would have to be developed before the sulfur monochloride-chlorine reagent could be employed for the production of thorium tetrachloride.

A procedure was developed for the purification of thorium tetrachloride contaminated with high-melting impurities. Purification is achieved by filtering the molten chloride at 900°C under 4 to 6 psig pressure through molybdenum wool supported on a fritted Inconel disk. This procedure has been effective in removing 98 per cent of the solid impurities.

The reduction of thorium tetrachloride with metallic sodium is conducted in a closed retort. Several modifications have been made on the retort to allow the addition of sodium vapor at a controlled rate. The sodium is vaporized into the reaction zone from a separate crucible supported above the reduction crucible. It is expected that this modification will significantly reduce the 30 per cent sodium excess previously required.

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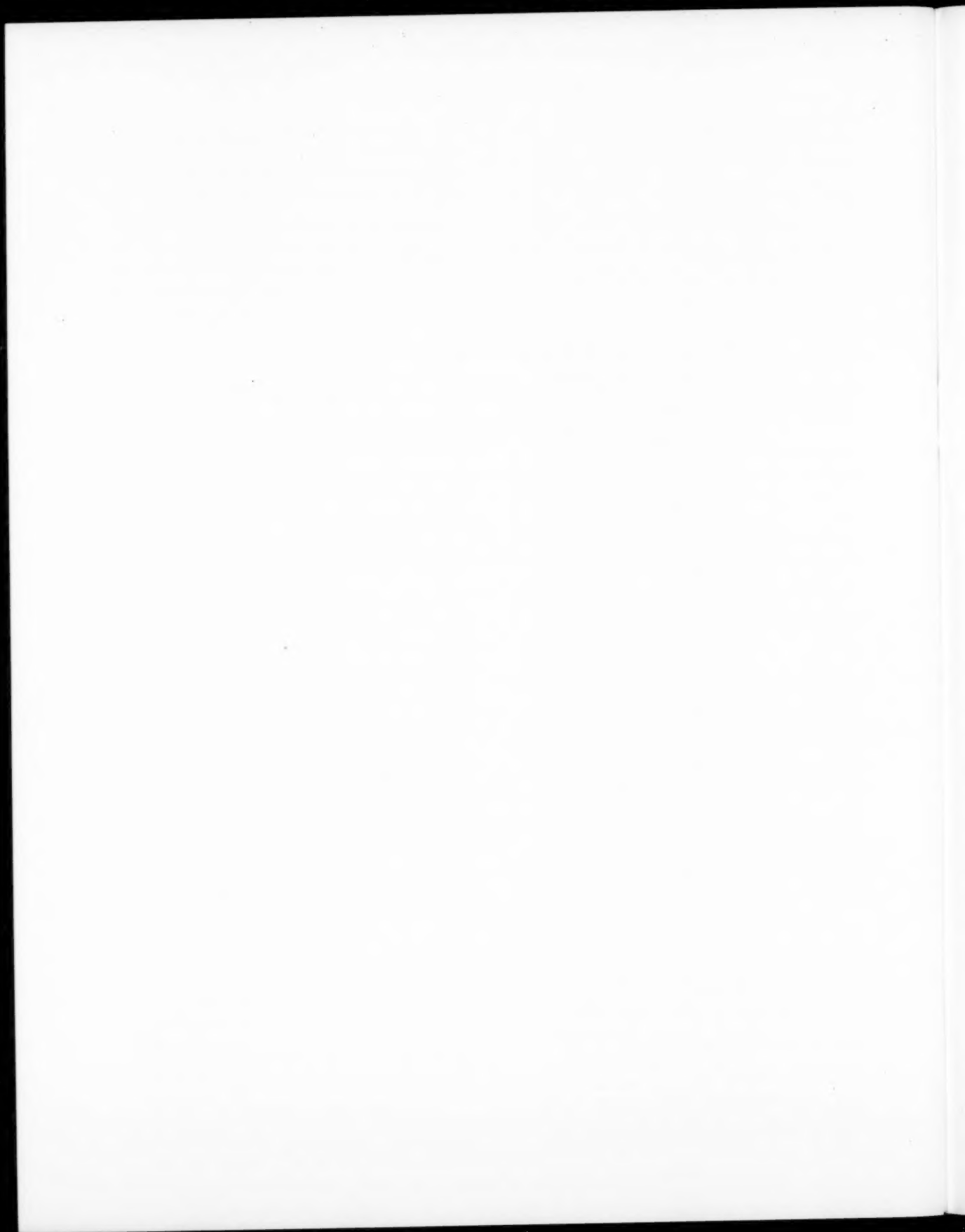
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